Published Monthly. Price, $5.00 per Annum.

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

VOL. XVIII.—NO. 6.

JUNE, 1896.

EDWARD HART, Editor, J. H. LONG, THOMAS B. OSBORNE,
COMMITTEE ON PAPERS AND PUBLICATIONS.

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EASTON, PA.:
CHEMICAL PUBLISHING COMPANY.

Entered at the Post Office, Easton, Pa., as Second Class Matter.

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PAPERS ACCEPTED FOR PUBLICATION:

Notes on the Electrolytic Determination of Iron, Nickel and Zinc. By H. H. Nicholson and S. Avery.

The Preperation of Trimethyl-amine from Ammonia. By Hermann Fleck.

The Value of Leather Refuse. By T. B. Lindsey.

Photometric Method for the Qualitative Determination of Lime and Sulphuric Acid. By J. I. D. Hinds.

The Chemistry of the Cactaceae. By Ervin E. Ewell.

Issued with June Number, 1896.

Proceedings.

COUNCIL.

Prof. H. H. Nicholson, Lincoln, Neb., has been elected a member of the Council, to take the place left vacant by the election of Dr. C. B. Dudley to the presidency of the Society.

The Council has voted to accept the invitation to hold the winter meeting at Troy, N. Y., on Tuesday and Wednesday, December 29 and 30.

The New York Section has asked that a committee be appointed to unify the methods of color comparison and report on a standard for measurement of color in potable waters. The Council has agreed to the formation of such a committee and named the following persons to act as members: A. R. Leeds, Wm. P. Mason, Thomas M. Drown.

NEW MEMBERS ELECTED MAY 11, 1896.

Bowman, J. W., Green Island, N. Y.
Hunziger, Dr. Aug., care Weidman Silk Dyeing Co., Paterson, N. J.
Yates, J. A., Williamsburg, Ky.

ASSOCIATES ELECTED MAY 11, 1896.

Meade, Richard K., Longdale, Va.
Pilhashy, Benjamin M., 1058 Cutter St., Cincinnati, O.

CHANGES OF ADDRESS.

Dodge, F. E., 316 Bowne Ave, Flushing, N. Y.
Hays, Joseph A., 147 So. 18th St., Pittsburg, Pa.
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Tonceda, Enrique, care Troy Steel Co., Troy, N. Y.

ADDRESSES WANTED.

Gallaher, Phil. C., formerly of Leadville, Colo.

MEETINGS OF THE SECTIONS.

CINCINNATI SECTION.

The regular meeting of the Section was held Wednesday evening, April 15th.

Dr. S. Waldbott presented a paper on "The Assay of Ipecac," in which he outlined the various methods for the alkaloidal assay of crude drugs and gave some results obtained by applying the Lloyd method for the assay of fluid extracts, to the determination of emetine in ipecac root; with some slight modification, Dr. Waldbott thinks good results may be obtained.

In a paper on "The iodoso- and iodo-compounds and iodonium bases, Dr. John McCrae gave an interesting account of some of the work he had done on these compounds, under the instruction of Victor Meyer.

NEW YORK SECTION.

The New York Section held its usual monthly meeting in the chemical lecture room in the College of the City of New York on Friday evening, May 8, with about fifty members present, Dr. Peter T. Austen, presiding. In response to inquiries regarding the progress made by the committee appointed to canvass the matter of the organization of a chemical club, Prof. Austen stated that in accordance with the instructions given, it had increased its numbers to fifteen and had held several meetings, to one of which the members of the New York sections of the American Chemical Society and of the Society of Chemical Industry, as well as manufacturers and gentlemen interested in the science and art of chemistry, business men and friends of chemistry were invited. The meeting was full and enthusiastic. The committee was instructed to increase its number to fifty or more and to push the organization of the club as rapidly as possible. The committee had held another meeting and added a large number of names of prominent chemists, manufacturers, and business men to the list. The general opinion seems to be that the initiation fee should be fixed at $25, and yearly dues at $25. It is the intention, while in no way hampering or restricting the evolution of the Chemical Club, which many of the more enthusiastic supporters of the movement predict, to start the club in a conservative and economical way, and not to exceed

the pecuniary limit which shall be decided upon after careful deliberation. It appears that there is not in existence in this or any foreign country any real chemical club, as differentiated from a chemical society. It is believed that the science and art of chemistry furnish so much that is characteristic that a chemical club may easily be made a unique organization. The members of the committee of fifteen are Prof. A. A. Breneman, Dr. A. P. Hallock, Prof. Peter T. Austen, Dr. W. McMurtrie, Prof. Morris Loeb, Prof. C. A. Doremus, Dr. E. R. Squibb, Dr. J. H. Wainwright, Mr. A. H. Mason, Mr. S. W. Fairchild, Mr. W. H. Nichols, Mr. W. J. Matheson, Mr. T. F. Main, Prof. A. H. Sabin, and Dr. C. F. Chandler.

Dr. A. R. Leeds, of Stevens Institute, read a paper on the "Bacteria of Milk Sugar." The author finds that the morphology, classification, physiology, and botany of bacteria are so rudimentary and unsatisfactory that the most valuable methods of bacteriological investigation are still of a chemical nature, and the advances to be made in the near future are to be looked for mainly on the chemical sides of the subject.

The author was interested to note in the progress of his work that precipitated zinc hydroxide, which is generally considered amorphous or gelatinous, is really crystalline.

Dr. H. W. Wiley, of the United States Department of Agriculture in Washington, offered a paper entitled "Recent Advances in Milk Investigations." In the absence of the author the paper was read by Dr. William McMurtrie. It treated of the bacterial theory of milk decomposition, the composition of woman's milk as compared with cow's milk, and the relative value of the two for infant food, and of the commercial standards which should be fixed for the milks sent to the city markets.

The author reviewed the work of Söldner regarding the proteid content of human milk, and quoted the figures given by authority for the average composition of human milk, as follows:

	Per cent.
Proteids	1.52
Fat	3.28
Sugar	6.50
Ash	0.27
Citric acid	0.05
Undetermined	0.78
Total dry substance	12.40

The undetermined substances, 0.78 per cent., are mostly nitrogenous bodies not generally found in cow's milk, and for this reason cow's milk can never be so diluted or altered as to properly supply the natural nutriment of the infant.

Söldner follows the method of Munk for determination of proteids, regarding as non-proteid matter those nitrogenous bodies not precipitated by tannin in presence of common salt. In woman's milk these amount to nine per cent. of the total nitrogenous constituents, and in cow's milk to about six per cent.

The author then discussed the view of Bechamp that milk derived from healthy animals is capable of spontaneous alteration, which consists in the development of lactic acid and alcohol and the development of curds in those milks which contain caseinates produced by the precipitating action of the acids formed. Oxygen and the germs present in the air are held to have nothing to do with this alteration of the properties of milk. The general conclusion reached is that microorganisms, such as vibriones and bacteria, are developed by a natural evolution from the microzymes, even in milk which has been boiled.

The surprising results of Söldner and Bechamp should lead to new studies of bacterial action in milk. If it should prove true that milk contains autogenetic germs for its own change, and that by the development of these germs into vibriones and bacteria, the natural souring takes place, it will be necessary to change completely the common view respecting these processes.

The author further discussed the commercial standards for the composition of milk, declaring that the value of milk, both for butter and cheese making, should be gauged by its content of butter fat, denouncing the claim of dealers that any milk from a healthy cow should be sold without legal restriction, no difference what its content of fat may be, and recommending that the minimum standard for fat content of milk supplied for human consumption should be placed at three per cent. or higher.

Dr. Leeds considers that in judging of the figures of Söldner presented it is important to be informed of the conditions under which the samples for analysis were taken and the quantity used for analysis, particularly for the determination of such constituents as citric acid and the undetermined substances. Samples

of woman's milk usually available are too small for such minute determinations. Regarding the content of proteids, the figures of Söldner do not vary widely from those previously found and reported. One hundred samples of woman's milk examined in New York gave an average of less than two per cent., with variations of 0.75 per cent. to 4.75 per cent. The only explanation of the very low figure of Söldner is that only partial secretion was available. The figure 1.52 given is not surprising.

That the various bodies secreted from the blood should be present is generally accepted. Variations in the composition of the milk, due to emotional influences, such as nervousness, excitement, fatigue, fright, anger, etc., are well known.

The fat and total solids given in the analysis are surprisingly low.

Dr. Eccles questioned the declaration that modified cow's milk was not a proper food for infants. Constant experience, forced by necessity, shows that it supplies excellent nutrition for infants.

Prof. Marston Bogert, of Columbia College, read a paper on "Normal Heptyl Thiocyanate."

The steps followed by the author in preparation of heptyl thiocyanate are as follows: Production of heptyl alcohol from oenanthol by reduction with zinc dust and acetic acid, conversion of the heptyl alcohol into the bromide, and addition of the bromide to boiling alcoholic solution of potassium thiocyanate. The yellow oil finally obtained washed free from potassium thiocyanate, dried with calcium chloride and distilled, all passed over between 230° and 234° C.

Normal heptyl thiocyanate is a colorless, mobile liquid, having a slightly alliaceous but rather pleasant odor and a specific gravity of 0.931 at 15° C.

Dr. Austen exhibited an apparatus for lecture demonstration of the properties of the heavier gases.

WASHINGTON SECTION.

A regular meeting was held Thursday, March 12th, 1896, with President Dr. de Schweinitz in the chair. There were

thirty-five members present, and Dr. Andrew Stewart was elected to membership.

Mr. F. P. Dewey read a paper on "The Refining of Lixivating Sulphides." Dr. Dewey's paper reviewed the leaching process and the treatment of sulphide precipitates produced. He described the sulphuric acid process of treating the sulphides, in which they are treated in strong sulphuric acid to convert the sulphides into sulphates, after the charge is treated with water, the silver precipitated by copper and melted, the copper sulphate crystallized. In the 1894 run of the Marsac Refinery, 116,519½ pounds of sulphides, carrying 572,544.4 ounces of silver by the corrected assay were treated, and 574,623.26 ounces of silver were returned, showing a plus clean up of 2,073.81 ounces, or 0.36 per cent. 96.29 per cent. of the product was in the form of bars, averaging 999.4 fine in silver, no gold.

Professor H. W. Wiley and E. E. Ewell read a paper[1] on "The Determination of Lactose in Milks by Double Dilution and Polarization."

Professor H. Carrington Bolton read a paper on "Berthelot's Contributions to the History of Chemistry," reviewing his "Collection des Alchimistes Grecs," (Paris, 1887; 3 Vol. 4to), and his "La Chimie an Moyen Age," (Paris, 1893; 3 Vol. 4to), showing their scope, analyzing their contents and indicating the important changes in chemical history resulting from Berthelot's studies.[2]

In the discussion of Dr. Bolton's paper, Dr. Wiley referred to the fact that the Phoenicians, as early as 1200 years before Christ, became famous by reason of the remarkable dyes which they produced, and that they were derived from a colorless substance found in certain mollusks, which, when exposed on fibers to the light, turned green, then red and purple. He referred to the fact that on the continent of Europe many scientific men had also become famous in politics, and among them preëminently Berthelot and Virchow. Berthelot was at least one official chemist who had attained political distinction, and his career might be imitated with advantage to the public service by some

[1] This Journal, 18, 428.
[2] This Journal, 18, 466.

American scientists; and we should not despair of looking forward to the day when chemists should at least be members of the Cabinet, if not Presidents of the United States. He thought Berthelot was particularly well suited to write of the alchemists, because some of his views would do credit to the wildest vagaries of the alchemists, especially his notion that the art of the chemist in the synthesis of foods, would in the near future render the practice of agriculture unnecessary. But we should not criticise a great man because of his vagaries, and after all it may be true that insanity is the highest type of genius.

The topic of discussion for the evening was "Style in Chemical Books and Papers." Dr. Wiley opened the discussion by saying there are many problems that present themselves to authors of scientific work. Some of these are of vital importance, while others are mere matters of taste. Not having expected to discuss the question on this occasion, he would confine himself to the minor topics. He suggested that there should be some uniform systsm of abbreviation employed, and for his part preferred very much small letters without periods. The introduction of capital letters in abbreviations marred the appearance of a book, and appeared to be entirely unnecessary. He thought perhaps some abbreviation of common metric terms would prove advantageous; for instance, the writing of the words cubic centimeters repeatedly not only requires a great deal of space, but the repetition of the term becomes tiresome. Some short word might be used to represent this magnitude, as, for instance, cubics. It would be well for chemists to agree upon some such system, provided the system were rational and easy of application.

Another question which often arises is in regard to the agreement between the noun and the verb, as, for instance, should we say 100 grams of iron are, or 100 grams of iron is? Another minor point is in the writing of numerals; whether they should be written out or the Arabic numerals used. He has adopted the plan of writing out in full numbers below 100, and placing the Arabic numerals for 100 and above. This was an arbitrary division, however, which might well be changed if some agreement could be reached in regard to it.

It appears that most scientific writers are so eager to express the truth or fact which they wish to convey that they lose sight altogether of the style in which the expression is made, and, as a result, their sentences become involved, and their meaning far from clear.

Another point which merits discussion is in the use of proper names to indicate any apparatus or process known by the name of the inventor. He preferred in such cases, where the personal idea had been lost, to use no capital, but to write the name of the apparatus or process with a small letter, as, for instance, a gooch or an erlenmeyer. The same is true of materials or reagents with geographical adjectives, as for instance, german silver and canada balsam, both of which should be written with small letters, just as the French, without disparaging the great Emperor, write the name of the coin napoleon with a little n or as we write telford or macadam for the name of a road.

Chemists should be careful about "take." It is not elegant to say "take five grams and place in a dish." "Place five grams in a dish" is entirely sufficient. In one work on chemistry he found the author directing the analyst to "take twenty-five grams of Glauber salts" with a big g. "Weigh out" is inadmissable. We do not weigh out, nor in, nor on, nor under. We simply weigh. In measuring it is not necessary to say weigh, as the chemist knows enough to use the balance without specific directions. A typically unnecessary form of expression and one not impossible to find is "take barium chloride, weigh out five grams, dissolve in water and filter off the insoluble residue."

Above all, the scientific writer should avoid indulging in fine writing. Plain, unvarnished statement of fact in a clear, lucid manner is what we should strive for. An example of how not to write is the following:

"For not only does the soil make possible a very much greater profusion of land life than could otherwise exist, but it has also played an extremely important part in that long-continued never-ending, and sublime process of evolution whereby, as lands have insensibly changed into sea and seas into land, as mountains have risen so slowly and silently out of level plains as to spring their broad arches directly across wide rivers to the height of a

mile and yet leave their course unaltered, as climates have changed from cold to warm or from wet to dry, both plants and animals in this great drama of the world action have been enabled to change, not simply their costumes, but, if the exigencies of the new scene demanded it, legs for fins or even abandon them altogether and crawl upon their bellies through the grass."

Professor Bolton said he thought one's grammar school education must have something to do with style in writing. Great labor is expended nowadays upon abstracts from foreign publications. He thought there should be a different method of treating them. The results might be presented without giving the steps by which they are reached. He thought that no one could depend entirely upon the abstracts, but have to refer to the original papers for details.

Professor Seaman said he was glad the subject was brought up; he thought some chemists had an idea that the English language is sacred, and that no changes should be made in it. This feeling must be met. He said that most persons read by words, and not by letters, and if a word has not the usual appearance to which we are accustomed, our first impression is that it is wrong, and hence he feared that no changes, however judicious, would seem agreeable. As to the agreement of collective nouns with verbs, Goold Brown concluded that the only principle to be followed is euphony. When the best grammarians cannot formulate rules, uniformity can hardly be expected. As to the use of small letters instead of capitals, the various changes that are going on in the language generally ought to be considered. The councils of biological societies have agreed that small letters should be used. Up to a few years ago specific names derived from proper names were begun with capitals, but now the small letters are used. As to the abbreviations used for weights and measures, he said no system had universal assent. Physicists and mechanicians have in use a long series of abbreviations for linear, areal and cubic measures. In three of the most important German chemical works, including the "Berichte," small letters are used, for the liters (l); for the grams (g); and for cubic centimeters (cc.), and he would be in favor

of adopting these, but unfortunately the pharmacists and physicians who are endeavoring to introduce them into their arts, have agreed upon the capital G and small r for gram, and capital C and small c without a point between them for cubic centimeter. Remsen in his first edition used cc., g., and l. Which are chemists to follow? The French do not use habitually any abbreviations. Some chemists, unfortunately, have not adopted the new spelling.

Professor Clarke said that a friend who wished to become a journalist, had consulted a newspaper man, and the advice he received was simple—"Have something to say and say it." Sometimes the writer is not sure as to what he wishes to say, and he tries to say something else, and his writing becomes involved. Another fault which was observed, especially in those who have just returned from abroad, was that everything that has ever been written upon the subject is given in an article, and the discovery of the authors is either buried in the mass or occupies a very small place at the end of the article. He thought a logical order should be followed, and an effort should be made to state what is said, simply and clearly. He thought Steele's "Fourteen Weeks in Chemistry" was a model of bad style.

Professor Munroe said that so far in the discussion there was apparently very little difference of opinion. He read the following from an article in "Science." "If we hear a baby crying with two ears, are we to think it is twins?" as an example of style in a scientific article. He thought this illustrated Professor Clarke's remarks about having something to say and saying it. Professor Munroe thought that the question of style had to be considered from two standpoints: that of the manual or text-book, and that of the technical or scientific paper. Abbreviations that might be properly included in the latter, should not be introduced in the former until they have long been used in technical literature. He was especially doubtful as to the advisibility of changing the adjectives to the substantive as a "gooch, a bunsen, a ruhmkorff, or a wiley," and the latter suggests that where one is as fertile as our distinguished associate, there may be a difficulty in determining which one of his many devices shall be called a "wiley."

Dr. Fireman said he did not agree with what had been said as to abstracts. Many papers are not accessible, and possibly only one journal could be obtained. With a good abstract the description of a process may be of use. Neither did he agree with the idea that an historical sketch should be introduced. He thought a summary was frequently of greater use. They are generally brief and give valuable references.

Dr. de Schweinitz closed the discussion by saying that he agreed with Professor Munroe that the style should differ in text-books and in technical papers. What is proper in one is not so in the other. He thought that abbreviations should be dropped as the purpose is to make what is written useful to all, and he thought the ideas and the statements should be expressed as simply and clearly as possible.

A regular meeting was held Thursday, April 9, 1896, with the the President, Dr. E. A. de Schweinitz in the chair, and thirty members and ten guests present.

The minutes of the eighty-seventh meeting were read and approved.

A letter from Dr. Salmon, inclosing a circular letter from the Director of the Pasteur Institute in Paris was read, asking the society to appoint a member to represent it upon the committee to raise funds for the erection of a monument in Paris to Pasteur. The President, Dr. de Schweinitz, was unanimously elected to represent the Chemical Society upon this committee.

There being no further business the reading of papers was proceeded with.

The first paper of the evening was by Mr. V. K. Chestnut upon "Some Vegetable Skin Irritants and their Chemical Composition." The paper consisted of a review of the work of Dunstan and Miss Boole on Croton Oil, and of Pfaff on Toxicodendrol, a new oil-like body from the poison ivy, *Rhus radicans;* together with an account of some vesicating plants which have been but little studied. Specimens of this plant were exhibited and the effect of an alcoholic solution of lead acetate as an antidote to Rhus poisoning was illustrated by experiments carried

out by the writer on himself. These experiments also showed conclusively that toxicodendrol was the vesicating principle of the poisonous species of Rhus. Discussion was by Messrs. Tassin, Munroe, Cutter, Stewart, Fireman and de Schweinitz. Mr. Tassin asked whether it was the lead acetate or the alcohol that is the antidote. Mr. Chestnut answered that the alcoholic solution of lead acetate is the best remedial agent. If the oil is kept long enough on persons supposed not to be susceptible, they will be poisoned; the poisoning may take place at the end of twelve hours, or not for five days. Portions of the skin that are thick are not so easily affected as are those where it is thin. Professor Munroe gave his experience as to nitrobenzol, which he had used in considerable quantity, and to which he and the workmen were exposed; it was inhaled as vapor, and came in contact with the skin, but no one was poisoned. The vapor is suffocating, but the workmen soon became accustomed to it. All the books, however, state that it is poisonous. Mr. Cutter said that he could uphold the books, as he had experienced its poisonous effects; he had rigor, fever, chills, and palpitation of the heart, and was unconscious afterwards; the effects lasted for three days, and the smell even now would affect him. Dr. Stewart gave his opinion of its poisonous effects upon the skin; in his own case it had caused an eruption that lasted three or four hours. Dr. Fireman thought that different effects might be produced by vapors and by the liquid; he referred to the effect of hydrofluoric acid vapors, which are not poisonous in any degree, although the liquid was well known to be very poisonous. Professor Munroe thought there might be differences in the substance. Dr. de Schweinitz thought that possibly it was impure in the cases cited by Dr. Cutter and Mr. Stewart.

Mr. Ewell read the second paper of the evening on "The Effect of Acidity on the Development of the Nitrifying Organisms," by E. E. Ewell and H. W. Wiley.

"While it has been known for many years that active nitrification occurs only in the presence of some basic substance capable of neutralizing the free acid as fast as it can be formed, very little time has been devoted to the study of the exact degree of acidity that the nitrifying organisms can endure. As

the authors had some forty samples of soil at their disposal during the last year for other purposes, it seemed wise to improve the opportunity to test the influence of acidity on the nitrifying organism contained in the soils from various parts of the country. Tests were made with forty-four different soils, from twenty-two states and territories. The results showed great uniformity in the relation to acidity of the organisms contained in the various soils. Excluding five tests in which no nitrification exists, and five tests in which it was excessive because of the calcareous nature of the soils used for the seeding of the cultures, the average amount of nitrogen nitrified was twenty parts per million; the minimum result of the thirty-four tests included in this average was eleven, and the maximum twenty-five parts per million. The tests are to be repeated with pure cultures of the nitrifying organisms of the same soils. This series of experiments was made as a study of the nitrous organisms only, but the results show that the nitric organisms are not more sentitive to acidity than the nitrous organisms, the final product being nitrate in nearly every case.

Dr. de Schweinitz, referring to the action of acids on the growth of bacteria, said they seemed to be able to accommodate themselves to their environment, especially in the case of the tuberculous bacillus, and after a time they seemed to grow better in an acid medium than in any other, though at first they needed coaxing.

The third paper of the evening was on "The Chemistry of the Cactaceæ," by E. E. Ewell.

Until very recently other species of cacti than *Cereus grandiflorus* and a few related species have generally been regarded as devoid of constituents of pharmacological value. These and other species, have been used in medical practice in the countries in which they grow, but their use has rarely extended to the more civilized nations. Species of the genus *Anhalonium* have long been used for curative and ceremonial purposes by the Indians of Mexico, and the southwestern parts of our own country. They found places in the Mexican pharmacopœia of 1842, under the name of "pellote," or "Peyotl," but have been omitted from the later editions. The dried aerial portions of

species *Anhalonium* figure in the commerce of our southwestern border under the name "mescal buttons." The species of this genus have been the subject of scientific investigation by at least three groups of persons during recent years: First, a group of persons at Berlin, where the work was begun by Dr. L. Lewin, the crude material being supplied to him by Messrs. Parke, Davis & Co., of Detroit; second, a group of persons at the Pharmacological Institute at Leipsic, where the work has been conducted by Dr. Arthur Heffter; third, a group of persons in this country, centering in the Bureau of American Ethnology, and including as associates the Division of Chemistry of the United States Department of Agriculture for Chemical studies, Drs. Prentiss and Morgan for a study of physiological properties, and the Botanical Division of the United States Department of Agriculture for the settlement of botanical questions.

Lewin reported the presence of an alkaloid in *Anhalonium lewinii* in 1888. He has given this the name of anhalonin and made an extended report on its physical, chemical and physiological properties in December, 1894. He has also found evidence of physiologically active substances in the related species.

In August, 1894, Heffter reported the presence of a poisonous alkaloid in *A. fissuratum*, to which he gave the name anhalin; he found an extract of *A. prismaticum* to be physiologically active, but did not have sufficient material for a more extended study; he separated an alkaloid that he named pellotin from *A. williamsi*; in *A. lewinii* he found evidence of the presence of three alkaloids, the description of the first of which accords with the description of Lewin's anhalonin. He made an extended study of the chemical, physical and physiological properties of anhalin and pellotin.

In this country, the separation of the constituents of these plants, and the study of the action of the substances thus obtained as well as of the crude materials, upon men and the lower animals, were begun in the autumn of 1894, but before receiving the paper of Heffter. *A. lewinii*, in the form of "mescal buttons," has served as the material for these studies. Anhalonin and a second alkaloid have been separated in considerable quantity. These, as well as other constituents of the

drug, including one or more resins, are turned over to Drs. Prentiss and Morgan for physiological experiments, as rapidly as they are obtained in an appropriate state of purity. A complete chemical study of the constituents of the plant is in process, including those substances of interest to the vegetable physiologist as well as those of interest to the therapeutist.

The paper was illustrated with specimens of the cactus of different varieties from the Botanical Gardens and the Department of Agriculture. Mr. Mooney followed with a paper on "The Mescal Ceremony among the Indians."

The mescal plant is a small variety of cactus native to the lower Rio Grande Region, and about the Pecos River in Eastern New Mexico. The botanical name has finally been fixed by Professor Coulter as *Lophophora williamsi*. Mescal is the name by which it is known to the Indian traders, but it is not to be confounded with the other mescal (Maguey) of Arizona. The local Mexican name is *peyote*, a corruption of the original Aztec name, from which it would seem that the plant and ceremony were known as far south as the valley of Mexico, at a period antedating the Spanish conquest. Several closely related species are described by Lumholtz as being used with ceremonial rites among the tribes of the Sierra Madre.

The dry tops, when eaten, produce such marked stimulating and medicinal results and such wonderfully beautiful psychologic effects, without any injurious reaction, that the tribes of the region regard the plant as the vegetable incarnation of the deity, and eat it at regular intervals with solemn religious ceremony of song, prayer and ritual. The ceremonial and medicinal use of the plant was first brought to public notice by James Mooney in a lecture delivered before the Anthropological Society of Washington in 1891, as the result of studies made among the Kiowas and associated tribes of Western Oklahoma. As the ceremony is forbidden, and the trade in the plant made contraband upon the reservations, the investigation was a matter of some difficulty. In 1894 Mr. Mooney brought back a large quantity of the dried mescal, which was turned over to the chemists of the Agricultural Department for analysis, and to Drs. W. P. Prentiss and F. P. Morgan, of Washington, for

medical experimentation. The results thus far would seem to indicate that the Indians are right in asserting that they have discovered in the mescal a valuable medicine entirely unknown to science, and which will probably take its place in our pharmacopœia along with those other Indian remedies, quinine and coca. The ceremony and songs are briefly described by Dr. Mooney, whose full investigation of the subject will ultimately appear in one of the publications of the Bureau of American Ethnology.

Dr. Francis P. Morgan followed with a paper on the "Physiological Action and Medicinal Value of Anhalonium lewinii. ("Mescal Buttons.")" Dr. Morgan stated that the investigation had been intrusted to Dr. D. W. Prentiss, with whom he was associated. Experiments were tried and observations taken at regular intervals to determine the action of the entire button on the system. The most striking result was the production of visions of the most remarkable kind with eyes closed, and especially so in the dark. Changes of color were characteristic; tubes of shining light, figures, cubes, balls, faces, landscapes, dances and designs of changing colors were among the most persistent visions. They were hardly seen with the eyes open; in full dose no effect on the reason or will is noticed in most cases. There was direct stimulation of the centers of vision and dilatation of the pupils. About one-quarter of the quantity or three buttons, are sufficient to give the visions in the case of white men. Dr. Morgan detailed the experiences of different persons who had tried the experiments. In some cases there was slowing of the heart, from seventy-five to forty-five beats, followed by a rise to normal; there is also inability to sleep, and a loss of the sense of time—hours seem to intervene between words. The physiological action is not identical with that of any known drug, it is unlike cannabis indica, cocaine, etc. The constituents of the mescal buttons are being experimented with, but the investigations are still incomplete. Anhalonin causes increased reflex irritability and convulsions, like strychnine. It is evidently not the active principle; another constituent has been isolated whose action is widely different. It does not cause opisthotonos, nor tetanus, and has

no action like that of strychnine. A third principle has also been isolated. The resin is supposed to be the active principle and will probably be of use in medicine. The experiments are still being conducted and will be detailed later on.

Dr. de Schweinitz expressed the indebtedness of the Society to Mr. Mooney and to Dr. Morgan, and said that the further results would be of interest to the Society.

A regular meeting was held Thursday, May 14, 1896. The president, Dr. de Schweinitz in the chair, with twenty-three members present. Mr. Mayville W. Twitchell was elected as associate member and Mr. Charles N. Forrest as member. The president presented the following resolutions, endorsed by the executive committee, and the Society adopted them; the president and secretary were instructed to sign and transmit them.

WASHINGTON, D. C., May 14, 1896.

TO THE HONORABLE, THE PRESIDENT OF THE UNITED STATES SENATE.

DEAR SIR :—In view of the proposed legislation now before the Senate in the form of a bill entitled "An Act for the further prevention of cruelty to animals in the District of Columbia," which, however, is practically an act to limit, and eventually stop, all experiments upon animals in the District of Columbia, the Chemical Society of Washington, including among its members a number of the most prominent chemists in the country, desires to present to the Senate of the United States a formal and positive protest against the enactment of any legislation upon the subject of vivisection.

The laws at present on the Statute books of the District of Columbia, if properly carried out, will apply to all cases of cruelty to animals which exist in this District. The proposed bill is objectionable for very many reasons. The penalties prescribed for the infraction of the law are preposterous. An expert who did not happen to possess a permit from the District Commissioners for the performance of experiments upon animals might suddenly have placed in his hands material, the dangerous character of which could only be determined by an immediate experiment upon an animal. Should such a test be made without a license, though possibly the lives of hundreds of peo-

ple were involved, the experimenter would be subject to an enormous fine and imprisonment, for having in the interests of humanity inoculated a guinea pig, or a rabbit, or some other animal, without a formal permit from the District Commissioners.

While the majority of the members of our Society are not directly engaged in experiments in which animals are used, we know that in certain lines of work, toxicology, materia medica, biochemistry, and the like, animal experimentation is absolutely necessary for the advancement of knowledge.

The agitators of the proposed legislation have not been able to show a single instance of cruel experiments conducted in the District of Columbia, either in any of the laboratories, or medical colleges, or public schools, consequently there is no need for any law on the subject. Furthermore, Washington is becoming the center of education for the entire United States. Four large universities are located here; several more are in prospect, and the proposed legislation would hamper and eventually destroy all possibility for advanced postgraduate work in the biological science, and indirectly in all allied branches.

We therefore, collectively as a Society, and individually as members, desire to protest strenuously against any legislation on the subject of vivisection, deeming it to be unwise, unnecessary, and in direct opposition to the spirit which has for a number of years actuated the United States government to encourage the advance of science. We hold further that such legislation would be a direct contradiction of the well-known practical results that have already been obtained by scientific investigations conducted under the government, which have made possible the saving of many thousand dollars worth of property and many human lives.

Yours very respectfully,

[Signed] E. A. DE SCHWEINITZ,
Pres. Wash. Chem. Soc.

A. C. PEALE,
Secretary.

The president, representing the Society, as a member of the Pasteur Committee, reported that the committee had organized and was ready to receive subscriptions.

There being no further business the reading of papers was proceeded with, Vice President Bigelow taking the chair.

The first paper was by Mr. Frederick P. Dewey, on "Practical Analytical Accuracy."

The paper did not go into the means of securing accuracy, but dealt entirely with the results actually obtained when a number of chemists worked upon the same sample. Not very much has been published in this line, but sufficient has been done to show that the ordinary accuracy of analytical work is not what it ought to be and that there is room for much improvement.

The paper gave results from analytical symposiums published in the Transactions of the American Institute of Mining Engineers and the Proceedings of the Association of Official Agricultural Chemists. It was also somewhat historical in character in tracing the development of accuracy in some determinations.

The discussion of Mr. Dewey's paper was by Messrs. Bigelow and Clarke.

Mr. Bigelow said that Mr. Dewey had selected the most accurate of the determinations by the Official Agricultural Chemists, but Dr. Dewey said he had simply taken those most nearly in his own line of work. He referred to Campbell's tables in the Journal and thought it was unfortunate that nothing was said as to the way they were obtained nor how he was led to adopt the various figures. He allows usually a small variation, but with silica he allows a variation of over one-half per cent, when large quantities are present.

Prof. Clarke thought that a great source of variation between different observers was due to the fact that too great faith was placed in the reagents. The work was not done with the same reagents and reagents are not always the same. Here, therefore, is a source of error.

Mr. Bigelow said he thought another source of error was due to the fact that the work was often done by students or subordinates and these results were published with the others.

Mr. Dewey said his paper was intended to exhibit what was actually obtained every day. He thought the assistant's work was not always the poorest. The principal very often was out of practice.

Dr. P. Fireman read a paper on "A New Mode of Formation of Tertiary and Quarternary Phosphines." When phosphoni-

um iodide is heated with ether in a sealed tube at 160°, for six hours, both ethyl groups of the ether became available for substitution, and these form the hydriodic salts of triethyl- and tetraethylphosphine according to these equations:

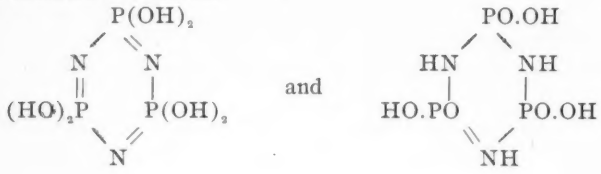
$$2PH_4I + 3(C_2H_5)_2O = 2P(C_2H_5)_3.HI + 3H_2O.$$
$$2PH_4I + 4(C_2H_5)_2O = 2P(C_2H_5)_4I + 4H_2O.$$

The author is at present occupied with the preparation of the homologous phosphines by the action of PH_4I and homologous ethers. He is also experimenting with a view of obtaining amines by the action of ammonium iodide or ammonium bromide on ethers or alcohols.

In the discussion of Dr. Fireman's paper Dr. Stokes asked if he had obtained any traces of primary or secondary phosphines. Dr. Fireman answered that primary phosphines are excluded and as to secondary phosphines he had at one time hoped he had obtained them, but he could not say with any certainty that he had. Dr. Stokes thought they might be recognized by the odor. Tertiary phosphines have the odor of hyacinths.

Dr. Stokes then read a paper on "Metaphosphinic Acids."

Dr. H. N. Stokes spoke on his investigation of the metaphosphinic acids, a series of acids having the general formula $(PNO_2H_2)_n$, *i. e.*, metaphosphoric acids in which one-third of the oxygen is replaced by NH. They are not, however, strictly speaking, derivatives of metaphosphoric acids, for while these contain a nucleus consisting of phosphorus atoms united by oxygen, the metaphosphinic acids, as proved by their formation from the chloronitrides $(PNCl_2)_n$, have a nucleus consisting of alternate phosphorus and nitrogen atoms. Two members of the series have been studied, *viz.*, trimetaphosphinic and tetrametaphosphinic acids, $P_3N_3O_6H_6$ and $P_4N_4O_8H_8$, derived from $P_3N_3Cl_6$ and $P_4N_4Cl_8$. Trimetaphosphinic acid apparently has the tautomeric formulas



Salts of both forms have been obtained. Under the action of acids, a successive decomposition is effected into $P_3N_2O_3H_7$, $P_2NO_6H_5$, $H_4P_2O_7$, and H_3PO_4. The second of these may be regarded either as $PO(OH)_2.NH.PO(OH)_2$ or $PO(OH)_2.O.PO<^{NH_2}_{OH}$, the former being supported by its derivation from $P_3N_3O_6H_6$, the latter by its easy conversion into pyrophosphoric acid. It presents a peculiar case of intra-molecular wandering of the nitrogen atom, possibly to be explained by a process analogous to Beckmann's transformation. (Particulars will appear in the American Chemical Journal.)

Dr. Fireman said the compounds appeared to him to be of similar constitution as cyanic acid and its derivatives; and also in regard to the tendency to polymerize and to appear in isomeric forms, there is a striking resemblance between both classes of compounds. He thought the results would be of interest in theoretical chemistry. As to the silver salts he asked Dr. Stokes if he had tried to prepare the esters.

Dr. Stokes said that a number of lactams are known that are stable, that open out or have open rings in which the tendency to break up is not marked. The tri acid is easily broken up but the tetra acid is not. In regard to the esters, he had tried to get them from the silver salts, but they are not like the organic ethers. They are very unpleasant to deal with and are coupled mixtures with which little can be done. He had thought of the analogy with cyanic acid and especially with the cyanuric acid compounds. Another theoretical point is the possibility of stereo-isomeric forms. When you have an oxime there are two isomers known. They split up differently — cis and trans bodies. He had not been able to find triphosphinic acid in any but two tautomeric forms.

Prof. Munroe said he was glad to see that the methods of organic chemistry were being applied to inorganic chemistry, but he would like to know why the linear form of the salts was written one way, and read in the reverse way in organic chemistry. He thought it was very confusing to students.

Dr. Stokes thought it was a matter of custom.

Dr. Fireman said he thought that the reason for writing the formula of the organic acid first and then that of the metal was due to the fact that the formulas of the organic acids were usually of a complicated nature and therefore it is natural to dispose of them first and that afterwards it is an easy task to fit in the symbol of the metal.

Prof. Munroe thought this was not the explanation.

Dr. Stokes said different men developed the two methods working from two different sides when a series of homologous compounds is written out. The constants are put down first and then those that vary. This was why he wrote them this way.

Prof. Seaman thought this the correct explanation. Ideas have a different arrangement with different people, normal to each one. He thought there was more uniformity in this country than anywhere else.

The Society adjourned until November.

VOL. XVIII. [JUNE, 1896.] NO. 6.

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE U. S. DEPARTMENT OF AGRICULTURE, NO. 20.]

THE EFFECT OF ACIDITY ON THE DEVELOPMENT OF THE NITRIFYING ORGANISMS.[1]

BY E. E. EWELL AND H. W. WILEY.

Received April 16, 1896.

FOR nearly two decades, both lay and scientific minds have been constantly perturbed by frequent announcements of the discovery of some new microbe that is seeking the destruction of ourselves or of our domestic animals. We have been warned to be on the alert for these deadly foes in the food that we eat, in the water that we drink, and in the air that we breathe. This general alarm has caused us to overlook many of the other important discoveries in the world of microscopic organisms. Indeed, the rapid development of our knowledge of the disease-producing organisms has been accompanied by an equally important advance in our knowledge of that multitude of microbes that are not only our friends, but are necessary to our existence. It is to one group of these more friendly organisms that we wish to ask attention. Passing over a host of species that are of importance in various agricultural industries, including those organisms that enable the farmer to draw upon the uncombined nitrogen of the atmosphere for an increase of his available nitrogenous plant food, we desire to consider the group of organisms engaged in the final stages of the process of transforming the nitrogen of dead animal and

[1] Read before the Washington Section of the American Chemical Society, April 9, 1896.

vegetable matter into an inorganic form suitable for the nourishment of the higher forms of plant life. It will be remembered that before the nitrogen of the fallen leaf or of a scrap of meat can be readily assimilated by the higher plants, it must undergo three stages of preparation by as many sets of organisms: first, the process of "ammonization," in which nitrogenous organic matter is decomposed, yielding as final products water, carbon dioxide and ammonia; second, the process of "nitrozation," in which the nitrous ferments oxidize the ammonia to nitrous acid; third, the process of "nitration," in which the nitric ferments oxidize the nitrous to nitric acid. The organisms of the first class, the ordinary putrefactive ferments, have been known since the work of Schwann and Schultze, reported in 1839, and have been made familiar acquaintances by the more recent work of Pasteur and others. More than thirty species of bacteria and twenty species of molds and yeasts were isolated from the soil and studied in regard to their ammonizing power in 1893 by Èmile Marchale, a Belgian investigator, the detailed results of whose experiments one of us (Ewell) has had the pleasure of placing before American readers in the form of a translation published in *Agricultural Science* about a year ago. Although our knowledge of this class of organisms has been greatly enlarged, their study from the standpoint of the practical agriculturist is still a very promising field of investigation.

The two remaining stages of the process, in which the ammonia formed by the putrefactive ferments is changed to nitric acid, constitute the process of nitrification, a term that is often used to include all three of the above transformations. Until very recently this was generally supposed to be a purely chemical phenomenon and quite independent of the action of living organisms. Pasteur, reasoning from analogy, had expressed the opinion that the process was dependent upon the activity of a living ferment, but it was not until the investigations of Schloesing and Müntz in 1877 that the dependence of the phenomenon upon living organisms was given experimental proof. Warington, in England, at once repeated these experiments and obtained results that left no doubt as to the nature of the process.

The existence of a nitrifying ferment having thus been demonstrated, the contest that at once began for the honor of its isolation was such a one as has rarely been seen in the scientific world. Warington and the Franklands, in England; Heraeus, Frank, Hueppe, Celli and Zucco, on the continent of Europe; Jordan and Richards, in America; all of these were prominent in this strife. As late as 1887, Frank asserted that the failure of the numerous attempts to isolate the ferment should be interpreted as evidence of its non-existence. For thirteen years the contest continued. The efforts of Warington, of the Franklands, and of Jordan and Richards, were just beginning to lead to tangible results, when, in 1890, a new worker appeared on the field in the person of Winogradsky, a Russian, working at Zurich. While many facts had been learned and many important observations had been made by the previous investigators, it was left for the worker last named to effect the first thoroughly satisfactory isolations of the nitrifying bacteria and to study them in pure cultures. These results were made possible by his finding a solid culture medium upon which these organisms grow well. Hosts of species had been isolated from the soil, from the air, and from natural waters by growth upon various solid media made by use of gelatine or agar-agar, but none of them possessed nitrifying power. Hence it had been concluded that the nitrifying ferment was unable to grow in these media, which were abandoned for the tedious dilution method. Winogradsky's medium was composed of gelatinous silica and nutrient salts. While its preparation is somewhat difficult and it apparently offers a pabulum for the development of a much greater number of microbian species than was at first supposed, nevertheless, it is the only medium available for the satisfactory isolation of the nitrous organisms. It is possible that this medium is also necessary for the isolation of some species of the nitric organism, but Burri and Stutzer[1] have recently studied a nitric ferment that thrives on ordinary peptone-gelatine. It is quite possible that these are the first workers that have ever given an organism growing upon peptone-gelatine an opportunity to grow in an inorganic solution containing nitrites; *i. e.*, in such con-

[1] Centralblatt f. Bakterologie u. Parasitenkunde, 1895, 1, 721–740.

ditions as would determine its ability to change nitrites into nitrates. As the demonstration of the inability of the nitrous ferment to grow upon ordinary peptone-gelatine preceded the discovery that nitrification is accomplished in two stages and by the action of two distinct ferments, it seems to have been taken for granted that the nitric organism is also incapable of growing upon the organic jelly.

We have treated the history of this subject somewhat at length, yet very briefly considering the extent of its literature. This has been done in order that what is to follow may be better understood. In the light of the researches and discoveries just outlined, the farmer must regard his fields as immense bacterial cultures. He must study their needs as well as the needs of the cultures of the higher plants whose conditions of growth he has been studying so long. In order that he may expect prompt, certain and remunerative results from the use of fertilizers containing organic nitrogen, he must make sure that his soil contains ammonizing and nitrifying organisms of the highest grade of activity, and must establish the closest possible approximation to those conditions that enable these organisms to render the greatest service in their respective roles: the conditions must be such that the process of ammonization proceeds with the smallest possible loss of nitrogen from the volatilization of the ammonia formed, or from the formation of uncombined nitrogen instead of ammonia; on the other hand, the conditions should be as unfavorable as possible for the activity of the organisms of denitrification, which reduce nitrates with the liberation of uncombined nitrogen.

Bacteria are very sensitive to the conditions under which they are grown; not only do changes in these conditions alter the rate and nature of their growth, but they also change the quantity and quality of the products formed during this growth. The principal conditions that have been found to greatly influence the growth of bacteria, are amount and quality of food, supply of moisture, the proportion of oxygen in the surrounding atmosphere, temperature, the degree of acidity or alkalinity of the medium in which they are grown, the presence of substances having a retarding or accelerating action upon their growth,

and the presence of rival or helpful species. Outside of the regions where irrigation is practiced, degrees of moisture and temperature are necessarily dependent upon meteorological conditions. In the case of the nitrifying ferments, increase of the aëration of the soil by thorough stirring has been shown to be very favorable to their highest activity. The most favorable quantity and quality of the various nutritive substances and of the other materials forming the soil, as well as the influence of the presence of other bacterial species, are still questions needing further investigation.

The proportion of alkali or acid in excess in the soil and in other media for the growth of bacteria has been shown to be a matter of the first importance. It is so constant a factor that it deserves consideration separately from the class in which it would logically fall, that of the substances having a retarding or accelerating action upon bacterial growth. The influence of the reaction of the medium upon the growth of bacteria has been very prettily demonstrated by various persons engaged in the quantitative determination of the bacteria in water. At the convention of bacteriologists, held in New York in June, 1895, George W. Fuller, of the Lawrence Experiment Station of the Massachusetts State Board of Health, presented a very interesting series of results upon this subject. We have taken the liberty to use an abridgement of one of Mr. Fuller's tables to illustrate the importance of this question.

Reaction. Cc. of normal alkali required to render one liter of the medium neutral to phenolphthalein.	Relative number of colonies per cc of water appearing upon plate cultures.		
	Sewage.	Merrimac River water.	Lawrence City filtered water.
40	6	1	2
35	16	3	3
30	45	4	8
25	64	55	46
20	100	100	100
15	106	89	92
10	101	54	60
5	98	46	43
0	86	38	35
— 5	87	26	31
—10	82	21	26
—15	55	9	15
—20	48	3	8
—25	56	1	7

The marked effect of slight changes in the reaction of the medium is rendered very apparent by this table. The most favorable reaction is one that is slightly alkaline to litmus, but still requires ten to twenty cc. of normal alkali solution per liter to make it neutral to phenolphthalein. When the acidity is either greater or less than this amount, there is a rapid falling off in the relative numbers of colonies formed.

While it was known for many years before the discovery of the nitrifying organisms, that the presence of some base is necessary to the activity of nitrification, there is very little known in regard to the exact degree of variation that can take place in the reaction of the materials undergoing nitrification without causing an interruption of the process. In the cultivation of the nitrifying bacteria in artificial media, it has been customary to add some carbonate that will neutralize the nitric acid as fast as it is formed. For this purpose, the carbonates of calcium and magnesium have been much more used because they are without influence upon the reaction of the medium until acid has been formed to decompose them. Warington[1] has made some experiments to determine the proportions of sodium carbonate and bicarbonate that can be used for this purpose. He reports that sodium bicarbonate can be used in the proportion of one to four grams per liter, that six grams per liter retards the activity of the ferments, and that eight grams per liter stops it entirely. The use of sodium carbonate was not attended with as good results, since one gram per liter was found sufficient to greatly retard the vigor of nitrification. This is practically all that is recorded in regard to the effect of acidity and alkalinity upon these organisms, except some statements in regard to nitrification in peaty and other soils sufficiently rich in humus to be acid in reaction. It has been reported that some soils of this type contain no nitrates whatever while in place.[2]

There are several ways of testing the effect of acidity upon the nitrifying bacteria. The soil itself may serve as a medium without sterilization, or it may be used after sterilization, the seedings being made from pure cultures of the nitrifying organ-

[1] *J. Chem. Soc.*, *1891*, 59, 529.

[2] Chuard, *Compt. rend.*, 114, 181–184.

isms or from mixed cultures of the soil bacteria; artificial media may be seeded from pure cultures of the nitrifying organisms, from mixed cultures of the soil organisms, or with a small portion of the soil to be studied. Each of these methods has its advantages and uses. In any case, the supply of ammonia must be maintained until the process of nitrification is arrested by the acidity of the medium. When the soil is used as a medium or as the inoculating material, the experiment becomes a test of both soil and organisms, as the acid formed can have no retarding action until all of the readily salifiable base of the soil has been satisfied. When the mixed organisms of the soil are used in media containing organic matter, acid may be produced by other organisms besides the nitrifying bacteria.

As we had some forty samples of soil at our disposal during the last year for other purposes, it seemed wise to improve the opportunity to test the influence of acidity on the nitrifying organisms contained in soils from various parts of the country. The medium selected for this purpose had the following composition:

Ammonium sulphate	0.943 gram.
Dipotassium hydrogen phosphate	1.0 "
Magnesium sulphate	0.5 "
Calcium chloride	trace
Water	1000.0 cc.

One hundred cc. of this solution were used for each test. Before the addition of the ammonium salt, one liter of this medium requires two and six-tenths cc. of normal solution of sodium hydroxide to make it neutral to phenolphthalein. The titration was made without the ammonium salt, as the indicator is not applicable in its presence. As for every equivalent of nitric acid formed during the nitrification of this solution, an equivalent of free sulphuric acid is liberated; the nitrification of fourteen parts per million of nitrogen causes an acidity of the medium equal to two cc. of normal alkali per liter.

A summary of the results of forty-four tests is given in the following table. Twenty-two virgin soils and twenty-two cultivated soils are represented, coming from twenty-two states and territories. The tests were continued for two months and the

figures recorded indicate the maximum number of parts per million of nitrogen nitrified during that time. In five cases no nitrification occurred; in four of these cases no nitrification occurred in the parallel tests made with the same soils and with the same medium to which calcium carbonate was added to neutralize the acid formed. In all but three of the tests the final product was entirely nitrate, showing that the nitric ferment was able to endure at least as much acidity as the nitrous ferment. In the three tests in which the nitrification was incomplete, there was only a small portion of the nitrite remaining unchanged to nitrate.

SUMMARY OF RESULTS.

In	5	cases	0	parts	per	million	of	nitrogen	were nitrified.
"	1	case	11	"	"	"	"	"	"
"	2	cases	14	"	"	"	"	"	"
"	4	"	15	"	"	"	"	"	"
"	5	"	18	"	"	"	"	"	"
"	10	"	20	"	"	"	"	"	"
"	5	"	22	"	"	"	"	"	"
"	6	"	25	"	"	"	"	"	"
"	1	case	28	"	"	"	"	"	"
"	1	"	40	"	"	"	"	"	"
"	1	"	42	"	"	"	"	"	"
"	1	"	70	"	"	"	"	"	"
"	1	"	130	"	"	"	"	"	"
"	1	"	170	"	"	"	"	"	"

Averages:

Of 44 tests 28 parts per million of nitrogen were nitrified.
" 34 " 20 " " " " " " ,

excluding five cases in which no nitrification occurred and five cases in which it was forty parts per million or more.

Remembering the numbers given above, we notice that the nitrification has stopped after the formation of an acidity equal to three to four cc. normal alkali, or when the reaction reaches five and a half to six and a half of Mr. Fuller's scale. It is quite possible that this extreme sensitiveness to acidity may account for the failure of attempts to grow these organisms upon ordinary peptone jelly.

In the case of the two peaty soils from the muck lands of

Florida, the results were twenty and twenty-two parts of nitrogen nitrified per million, which are very close approximations to the mean result of all the tests. The soils giving the excessive results of 130 and 170 parts per million were from Alabama, and examination has shown that they are both very rich in calcium carbonate. This, of course, explains the high results obtained.

We have "stock cultures" of the nitrifying organisms of all of these soils and hope to be able to report a repetition of these experiments with pure cultures, thus eliminating possible sources of error that may have resulted from the presence of the basic substances of the soils used as inoculating material in the series just reported. It is also desirable to determine the relative effects of various organic and inorganic acids upon the nitrifying organisms. This can only be satisfactorily accomplished by use of pure cultures. In regard to the effect of acidity upon the nitric ferments, but very little is known, except that, as we have observed above, they are not more sensitive to acidity than the nitrous ferments. The practice seems to have been to add an insoluble carbonate to the liquid media used for the growth of nitric organisms also, but we have found that this is unnecessary. The nitric organisms from all of the soils with which we have experimented, thrive well in a medium having the composition of the one given above in which sodium nitrite takes the place of the ammonium salt. There is, of course, no increase in the acidity of the medium during the growth of this ferment, as it merely changes nitrites to nitrates.

The organisms coming from various parts of the country seem to be very uniform in regard to their ability to endure acidity. If these results are again obtained when the tests are repeated with the pure organisms isolated from the different soils, the interpretation to be given to them is a very important one: these results are to be looked upon as evidence that we are to seek practical results in the study of the nitrifying organisms, not from a search for a peculiarly active species, but from a search for those conditions that are most favorable to the activity of these organisms in any given set of soil and climatic conditions.

These conclusions gain strength from the results of the recent

experiments of Burri and Stutzer,[1] in which they found that the mixed organisms from several samples of soil from widely separated sources assumed an almost constant nitrifying power after a series of cultivations in an artificial medium. Whether their results are to be interpreted as an evidence of constant nitrifying power in organisms from widely different soils when these organisms are cultivated in the same medium, or whether they are to be regarded only as another example of the extreme variability that bacterial species have so often been observed to exhibit, is only to be determined by extended experiments. Of high value for the confirmation of these, or of any other results obtained by means of artificial culture medium, is the re-inoculation of several soils with each of the organisms studied, noting the results during long periods of time. Both sterilized and unsterilized soils should be used for this purpose, as well as soils in which the chemical and biological conditions have been variously modified by artificial means.

We feel that the contribution that we have just made to the knowledge of this subject is almost lost in the vast unknown of the field that still remains to be explored, but this is offered as a note of the work that has been undertaken by us of attempting to make a comparative study of the microorganisms important to agriculture in typical soils from all parts of the United States. This note is not presented with any desire to preempt this field of study, for it is broad enough to monopolize the time and skill of many workers for many years to come.

STANDARD PRISMS IN WATER ANALYSIS AND THE VALUATION OF COLOR IN POTABLE WATERS.

By Albert R. Leeds.

Received April 16, 1896.

IN one of the first papers read before this Society and contained in its Proceedings, Vol. II, p. 1, for 1878, I have given an account of an instrument and a method for reading the quantities of ammonia obtained in nesslerizing, the instrument being termed a color comparator. It was designed primarily for this purpose only, and had its origin in the irregularities observable

[1] *Centralblatt f. bakteriologie u. Parisitenkunde, 1896*, 2, 105-116.

in the readings of the very minute amounts of ammonia obtained in the course of water analysis. It was subsequently found to be of great service in giving more precision to the measurement of color in potable waters, and it was used for this purpose and also for the estimation of the percentage of carbon in pig-irons, etc. The color struck by 0.01 milligram of ammonia was taken as the unit for natural waters.

The apparatus has been figured in the catalogues of the dealers for the past twenty years, and I need not describe it again here. It avoided the sources of error due to reading the tubes under different conditions and from the side, from the top and in different manners.

The light was reflected from a mirror, placed at an angle of 45°, down and through the middle of the tubes standing on the rack, and then by a second mirror placed below, but at right angles to the first, outward to the eye of the observer. The object was to compare the colors obtained in nesslerizing not with any one series of trial tubes prepared at the time and which might vary within wide limits, but with a coloring material contained in a wedge in connection with which the results of many readings could be plotted and so preserve a permanent standard of comparison. This wedge was placed below the aperture, next to the tube under comparison, but in order that the optical image might be similar in all respects, a tube filled with distilled water was placed above the wedge and the dark rings made by the light transmitted downward through the walls of this tube, made a part of the image also.

All that the eye then had to do was to determine whether the depth of color in two rectangular spaces, as seen in the lower mirror, each space being twenty-five mm. by ten mm. and separated by an interval of ten mm., was or was not equal. When the rack is full, which is the case in two duplicate nesslerizings, the whole of the results are before the eye of the observer at one and the same time, and twelve blocks of color strung along one after another in a horizontal line, are seen brilliantly lit up on a perfectly black ground.

But the difficulty was to obtain a suitably colored fluid to fill the prism. Naturally enough recourse was had in the first place

to the chromogenic metallic salts as being easiest to prepare of a definite strength, and as probably of the most permanent composition. To this end very many trials were made with mixtures of iron, chromium, nickel, cobalt, ferrocyanogen, gold and platinum, but all without success. When a solution gave a series of tints which were satisfactory for the lower end of the scale, it was unsatisfactory for the upper, and vice versa. Then mixtures of these salts with admixtures of coloring matters and with infusions of tea, coffee, etc., were tried and finally a solution of caramel corrected by anilin red showed as close a parallelism with the colors struck by the nesslerized ammonia as any combination experimented upon.

It was fully recognized at the time that none of these expedients fulfilled the conditions of complete parallelism of tint, permanence and ease of handling, that were desirable, and the attempt was made to substitute for the hollow wedge one of colored glass. Mr. Emil Greiner obtained many specimens of greenish-yellow, yellow and orange-yellow glass, and lent his skill in grinding them down into suitable long thin prisms. But they all failed at one or the other end of the scale, and when they were examined by the spectroscope and the difficulty was found to be due to a selective absorption of the color in the different parts of the prism, the attempt to make a satisfactory prism out of one kind of glass only was abandoned. Then thin sheets of differently colored glasses were taken, with the hope that by combination and superposition the changes of tint throughout the scale could be imitated. But at this time a very limited number of shades of color in glass could be obtained. At the present day, with the enormous development of the art of making and using glass for decorative purposes, the case is different. I am experimenting upon composite wedges, made up of wedges of different colors, and the results are promising. Certainly the obstacles to be overcome are not nearly so great as those which have been surmounted in getting rid by means of over-correction and under-correction of both spherical and chromatic aberrations in a lens. Similar composite glass wedges could be employed to estimate minute amounts of iron when a color reaction with a thiocyanate or ferrocyanide is utilized, or for

small quantities of copper or other color-giving substance.

We are only too familiar with the sources of error in the Nessler process, and every chemist at the outset of his work in water analysis is compelled to devote much time to their study. A very slight variation in the mode of preparation makes a great difference in the sensitiveness of the Nessler reagent itself. Potassium, mercury, chlorine and iodine form a large number of salts, and that their molecules are complex and constantly changing is shown by the gradual change of color of the reagent from its first pale greenish-yellow color to a light straw tint with a corresponding gain in sensitiveness. But even with a reagent which is duly sensitive in the lowest part of the scale, and with due care in seeing that the liquids are brought to a proper temperature, and with every minute precaution as to measurements, thorough admixture, etc., there still remains many uncontrollable irregularities. It frequently is the case that the color struck by 0.001 milligram of ammonia is even greater than that given by 0.002 milligram; that given by 0.002 about the same as that given by 0.003, and so on. On standing, the precipitates which settle out, are not uniform in composition, red tetragonal crystals, resembling mercuric iodide, being oft-times accompanied by dark green crystals resembling the mercurous salt. By making up a sufficiently large number of trial sets at one time, it is possible to pick out from them a series in which the differences of tint corresponding to five-tenth cc. of ammonia are, so far as the eye can judge, equal.

The same result is obtained by plotting the results of many readings on a permanent scale. As ascertained by comparison with such a scale, the sum totals of the readings are more accurate than those obtained by comparison with any one trial set made up of fluctuating and perishable members. When we consider that there is an increase both in the delicacy of the reaction and in the ability to read the color tint up to a maximum, after which both fall away again, it is probable that the most accurate method of reading would be to have a permanent scale, divided into equal parts, and to use the scale only for so much ammonia as corresponds to the differences of color which the eye is capable of estimating with certainty.

VALUATION OF COLOR.

As has been remarked above, it was not till after the color comparator had been proposed as a means of estimating the percentage of nesslerized ammonia, that the same scale was extended to the measurement of color in waters. The article in the Journal was reprinted with illustrations in the *Zeitschrift für analytische Chemie*, 17, *276*, and in the *Chemical News*, in the issue of June 7, 1878. In the issue of the latter journal for April 14, 1881, in their report upon the London water supply, Crookes, Odling and Tidy gave the following account of a similar method:

"For some time past we have been experimenting on methods of determining the colors of water, and we have this month adopted a process which, whilst it does not pretend to absolute accuracy, is a great improvement over the arbitrary 'degrees of tint depth' by which the color of water has hitherto been estimated. The process briefly is as follows:

"Two hollow wedges are filled, one with a brown and the other with a blue solution,[1] and these are made to slide across each other in front of a circular aperture in a sheet of metal. In this way any desired combination of brown and blue can be produced. Each prism is graduated along its length from one to forty, the figures representing millimeters in thickness of the solution at that particular part of the prism.

"On a level just below the prisms is a two-foot tube containing the water under examination, and having in front of it a circular aperture of the same size as the one in front of the prisms.

"The stand supporting the prisms and tube is placed horizontally in front of a uniformly lighted window. The observer, standing a little distance off, sees two luminous disks, the lower one illuminated by light, which has passed through two feet of water, and the upper one illuminated by light which has passed through the respective thicknesses of the brown and blue solutions.

[1] The solutions are made in the following way: *Brown Solution.* Dissolve ferric chloride and cobalt chloride in distilled water in such proportion that one liter of the solution contains 0.7 gram of metallic iron, and 0.3 gram of metallic cobalt. A very slight excess of hydrochloric acid must also be present. *Blue Solution.* Dissolve ten grams of pure crystallized copper sulphate in one liter of distilled water.

"By sliding the prisms sideways, one way or the other, it is easy to imitate with considerable accuracy the depth and tint of the color of the lower disk. A metal pointer affixed over the center of the upper disk shows on the prism scales the number of millimeters in thickness through which the light has passed to produce a color which corresponds to that of the water, and the results are recorded in the following way: Brown : Blue. Thus: "February 21, (New River), 20 : 21 means that on that date the color of New River water seen through a two-foot tube was represented by twenty millimeters of brown and twenty-one millimeters of blue solution."

Subsequently the board of London examiners abandoned the use of iron and substituted for it one of potassium dichromate.

Recently Allen Hazen, in the March number of this Journal, has advocated the use of a solution of platinic chloride, this constituent being of fixed strength, together with a solution of cobalt chloride to be added in accordance with the color sense of the observer. Possibly other chemists are employing still different solutions, and it is probably somewhat premature to expect at the present moment a concensus of opinions as to the best substances to be employed. In laying out the methods to be pursued in the examination of the waters submitted to the State Board of Health of Massachusetts (see their Report for 1890), T. M. Drown adopted the Nessler ammonia scale as the scale for color also. And in the January number of this Journal, E. H. Richards has given at length the reasons for adhering to this scale and her method of applying it through an intermediate set of colored natural waters, verified by fiduciary comparisons of certain points on the Nessler ammonia series.

In order that this renewed discussion may have the greater practical value, I shall venture to make the following suggestions:

1. That the unit of depth in the measurement of the color of water should be taken at 200 mm. This depth was used in the comparison tubes, which contain 100 cc. at the 200 mm. mark, for the reason that the same depth has already been adopted in the polariscope. Moreover, 200 mm. or eight inches, is a depth of water familiar in household use, while two feet is not, and

it is a unit that can be more conveniently applied to the unfiltered surface waters now in general use in this country, than the two-foot depth made necessary in gauging the filtered waters supplied to London and other European cities. With the general introduction of filtered waters in this country, three times 200, or 600, (which is very nearly two feet), could be used in measuring color in water that fell below 0.2° on the scale. The unit tube could be applied to waters showing between 0.2° and 2°. In order to preserve identity of conditions, which is of such fundamental importance in optical measurements, instead of diminishing the depth of the more highly colored waters, those between 2° and 4° could be diluted with an equal bulk of water and read in the unit depth of tube.

2. I would respectfully urge as a matter of priority and inasmuch as a very great number of measurements of color in this country are already so recorded, that the unit therein adopted which corresponds to the color struck by 0.01 milligram of nessnerized ammonia, should be retained. It may be said that for the reason already given this unit is one which cannot be precisely ascertained. But to compare lesser things with greater the same thing may be said of the meter; to rectify it in the manner originally intended, will prob bly never be attempted, and yet, at the same time, the meter is an universally accepted and well defined magnitude. Moreover, every time an ammonia determination is made, this unit must be ascertained and the readings for color are usually done at the same time as those of ammonia. Whether a scale is made with chromium or platinum or any other pure substance, there would be no difficulty in determining the weight of metal to be used to give the same color as that struck by 0.01 milligram of ammonia, within any such limit of precision as the eye is capable of measuring. Such a scale divided from 0 to 1 into ten equal parts and then the same divisions continued higher, could be used in the estimation of ammonia also.

3. Instead of using this scale directly, there would be great gain in using its equivalent in glass. If he desired, each chemist could test the glass scale by comparison with a fluid one made

by himself, but in daily use indestructable and properly compensated glass wedges have many advantages.

A METHOD FOR SEPARATING THE "INSOLUBLE" PHOSPHORIC ACID IN MIXED FERTILIZERS DERIVED FRON BONE AND OTHER ORGANIC MATTER FROM THAT DERIVED FROM ROCK PHOSPHATE.

By A. P. Bryant.

Received April 13, 1896.

DURING the year 1895 the wholesale price of rough bone was about $19.50 per ton in the New York markets. Ground bone brought $22.75 per ton, and ground Charleston rock averaged $8.12½ per ton. After allowing for the value of the ammonia, the phosphoric acid purchased in bone still costs considerable more than the same amount purchased in mineral phosphates.

Estimating 3.75 per cent. of nitrogen in the ground bone, wholesale cost 12.3 cents per pound, there would be $9.23 worth of nitrogen per ton. This value would make the phosphoric acid in a ton of ground bone cost at wholesale $13.52, when the same amount approximately of phosphoric acid in ground rock costs about $8.12½ per ton.

This cheapness of mineral phosphates has led to their very general use by fertilizer manufacturers instead of bone as a source of phosphoric acid.

While the so-called Available Phosphoric Acid[1] of the two may be of equal value, it seems wrong to classify the phosphoric acid of mixed fertilizers insoluble in the ammonium citrate solution at the same price in the two. The Connecticut State Station's Report "Trade Value," of the organic phosphoric acid is (average) five cents per pound, while in the raw ground rock it is but two cents per pound.

It has been urged that there is no means of telling whether the "insoluble" phosphoric acid in mixed fertilizers was derived from minerals, or from bone and tankage. It was for

[1] That portion soluble in a neutral solution of ammonium citrate, sp. gr. 1.09, digested at 65° C. for thirty minutes.

this reason that the experiments herewith described were undertaken.

The method employed depends upon the difference in specific gravity between bone and other organic matter and the mineral phosphates. The following are the specific gravities of some of the more important compounds found in bone and in rock phosphates:

	Sp. Gr.
Bone and other organic matter, less than	2.0
Gypsum	2.3
Aluminum phosphates	above 2.3
Iron phosphates	about 2.6
Silica	2.65
Calcium phosphates	2.9 to 35.5
Fluorite	3.2

For the separation of the bone and organic matter from the mineral matter, a solution of mercuric iodide in potassium iodide was employed. This solution was first proposed by E. Sonstadt[1] in 1873, and elaborated by Thoulet[2] in 1878. The solution, as prepared by the writer, is as follows: Seventy-five grams of potassium iodide are dissolved in 350 cc. of warm water, and 100 grams of mercuric iodide added. The solution is filtered and evaporated in a porcelain dish over a water-bath, until a crystal of pure gypsum, sp. gr. 2.3, comes to the surface. The solution is then diluted at 15.5° C. until the gypsum is of the same density as the solution, scarcely floating or sinking. The solution is now at specific gravity 2.3, and should be diluted to specific gravity 2.26 according to the formula $V' = \frac{V(D-D')}{D'-1}$ where V' is the volume of water to be added, V the volume of the solution, D its specific gravity 2.3, and D' the desired specific gravity 2.26. The specific gravity should be verified by use of the picnometer.

The separating solution should be placed in a small flask of about 100 cc. capacity, fitted up on the same plan as a wash bottle. The amounts given above will make about 100 cc. of solution.

[1] *Chem. News*, **29**, 127.
[2] *Compt. Rend.*, Feb. 18, 1878.

The tube for making the separation may be as elaborate as desired. A very good form is described by S. L. Penfield in the *American Journal of Science* for Dec. 1895. The following has given excellent satisfaction in these experiments. A glass tube, a broken burette for example, about one and three-tenths cm. internal diameter and twenty cm. long is connected by means of a short piece of rubber tubing, with a tube of similar diameter, closed at one end and about seven cm. in length. See Fig. 1.

The material to be separated is placed in the tube and fifteen or twenty cc. of the separating solution added, after which the tube is stoppered and shaken thoroughly. The sides of the tube are now washed down with more of the solution; after standing for five minutes, the bottom part or bucket should be tapped smartly to release any light portions carried down with the heavy material, and a jet of the solution blown against the matter floating at the top, to dislodge any heavy particles. The tube is then let stand till the solution is clear, all matter having gone to the top or bottom. This will usually take from forty minutes to an hour in finely ground mixed fertilizers or rock superphosphates.

Fig. 1.

The rubber tube is now tightly clamped with a screw pinch-cock, separating the heavy material from the light. A beaker is placed beneath the tube, and the lower tube or bucket is removed, the fingers being encased in rubber finger-tips, as the separating solution cracks the skin. The tube and contents are brought on a dry filter and the liquid filtered back into the supply flask. Water is then used, the first washings being saved and evaporated down to a specific gravity of 2.26 again. The light portion is treated in a similar manner, care being taken to get all particles out of the tube at the last.

At first it was not supposed necessary to have any fixed specific gravity, but as will be seen by the following table, it is

important that the specific gravity should be somewhere about 2.26. The exact reason for this is not in the province of this paper to decide, but seems to be owing to the low specific gravity of the aluminum phosphates.

The plan of the experiments carried on was to take a fertilizer known to contain nothing but organic matter as a source of phosphoric acid, and a mixture of South Carolina and Florida phosphates, both the raw rock, and the acidulated product. These were analyzed and then mixed in different proportions and treated with the separating solution.

In the first experiment two grams of the mixture were treated with 100 cc. of the the neutral ammonium citrate solution (sp. gr. 1.09), and digested for thirty minutes at 65° C., shaking every five minutes. After filtering, the dried insoluble residue was separated as carefully as possible from the filter paper and treated as previously described. As will be seen by reference to the table following, this method, though most desirable, was given up owing to the large proportion of phosphoric acid left on the filter paper.

The next attempt was to treat the mixed fertilizer directly with the separating solution, and was also abandoned owing to soluble matter in the fertilizers which destroyed the separating solution.

These two experiments showed two things clearly, that the fertilizer cannot be treated with ammonium citrate solution before separating, and that the matter soluble in water must be removed before separating.

To obtain this latter end and expose the minimum amount of filter paper, the inner tube of a fat extraction apparatus was used, such as was described by Prof. S. W. Johnston.[1] These tubes are used by the Storrs (Conn.) Agricultural Experiment Station, and are made for them by Whitall, Tatum & Co., New York. The tube is about fifteen cm. in length and two and five-tenths cm. internal diameter, slightly contracted at one end, which has a rim so that a piece of filter paper reinforced on the outside with cheese cloth, can be tied on. (Fig. 2.) The method is as follows :

[1] *Am. J. Sci.*, **13**, 190, *1877*

Two grams of the raw or mixed fertilizer are transferred to the "extraction" tube and extracted with nearly 250 cc. of hot water, as for water soluble phosphoric acid determination. The tube and contents are placed in a drying oven, and when thoroughly dry the filter paper is taken off and all matter carefully removed with a spatula and brush. Any fine sediment adhering to the glass may be removed by a rubber tipped glass rod.

Fig. 2.

The material is now transferred to the separating tube and treated as before described.

The light portion and heavy portion are treated separately with ammonium citrate solution, and the insoluble phosphoric acid determined in the usual way. That in the "light" comes from bone, tankage or other organic matter, that in the "heavy" from minerals.

The following is a tabular statement of the results of the experiments:

Material.	Total P_2O_5.	Insoluble P_2O_5.
Prepared mixed fertilizers[1]	10.75	2.56
Mixed Florida and Carolina raw rock	27.51	24.36
Mixed Florida and Carolina dissolved rock.	16.23	0.77

PERCENTAGE OF PHOSPHORUS PENTOXIDE FOUND IN THE HEAVY AND LIGHT PORTIONS AND LEFT ON THE FILTER PAPER.

No. of experiment.		Specific gravity.	Light.		Heavy.		Left on paper.	Total.	
			Theoretical.	Found.	Theoretical.	Found.		Theoretical.	Found.
	Treated with ammonium citrate before separating.								
1	Mixture A 1	2.46	1.28	1.79	12.18	8.33	2.66	13.46	12.78
2	Mixture B 2	2.46	1.28	2.02	0.39	0.43	0.44	1.67	2.89
3	Mixture A 1	2.46	1.28	1.83	12.18	8.33	2.66	13.46	12.82
4	Mixture A 1	2.35	1.28	1.52	12.18	9.68	2.66	13.46	13.86
5	Mixture B 2	2.35	1.28	1.66	0.39	0.49	0.44	1.67	2.59
	Separated before treating with ammonium citrate.								
6	Mixture B 2	2.22	1.28	0.93	0.39	0.70	trace	1.67	1.63
7	Mixture A 1	2.26	1.28	1.38	12.18	11.65	0.12	13.46	13.15

[1] Containing acidulated bone, tankage, dried blood, sodium nitrate and potassium sulphate.

No. of experiment.		Specific gravity.	Light.		Heavy.			Total.	
			Theoretical.	Found.	Theoretical.	Found.	Left on paper.	Theoretical.	Found.
8	Mixture C 3	2.26	1.28	1.63	6.28	6.03	0.06	7.56	7.72
9	Mixture B 2	2.26	1.28	1.18	0.39	0.65	trace	1.67	1.83
10	Mixture A 1	2.26	1.28	1.28	12.18	12.03	0.12	13.46	13.43
11	Mixture C 3	2.26	1.28	1.35	6.28	6.08	0.06	7.56	7.49
12	Mixture B 2	2.26	1.28	1.11	0.39	0.48	trace	1.67	1.59
13	Mixture A 1	2.26	1.28	1.24	12.18	12.07	0.12	13.46	13.43
14	Mixture C 3	2.26	1.28	1.15	6.28	6.09	0.06	7.56	7.30
15	Pre'd mixed fertiliz'r	2.26	2.56	2.51	....	....	trace	2.56	2.51
16	Dissolved rock.....	2.26	...	...	0.77	0.70	trace	0.77	0.70

1 Mixture A, 1.0 gram prepared mixed fertilizer.
" " 1.0 gram raw Florida and Carolina rock.
2 Mixture B, 1.0 gram prepared mixed fertilizer.
" " 1.0 gram dissolved Florida and Carolina rock.
3 Mixture C, 1.0 gram prepared mixed fertilizer.
" " 0.5 gram raw Florida and Carolina rock.
" " 0.5 gram dissolved Florida and Carolina rock.

Of the above analyses, the first five were tentative, the method and manipulation were experimental, and the results were unsatisfactory. They show, however, that a specific gravity of 2.46 or 2.35 is too heavy for the proper workings of this method, and that when treated with ammonium citrate solution before separation, at least twenty per cent. of the phosphoric acid is lost through the adherence to the filter paper.

The sixth analysis shows that a specific gravity of 2.22 is too light, and matter which should rise to the top sinks to the bottom. Nos. 7 to 14 show that the method as finally elaborated, is quantitative and apparently reliable and capable of being put into regular use as a method of testing the source of the insoluble phosphoric acid in mixed fertilizers. The attempt was made to treat first with ammonium citrate, and filter through the extraction tube above described, in order to expose less filter paper, but the solution would not filter at all.

No. 15 was a sample of mixed fertilizer containing acidulated bone, tankage, dried blood, sodium nitrate and potassium sul-

phate, and formed the source of the "light" phosphoric acid in the above experiments. When treated with the separating solution (after dissolving out salts soluble in water) everything rose to the top with the exception of a very small amount of some material, either calcium sulphate or silica, as there was no trace of phosphoric acid in it. The solution was perfectly clear in ten minutes.

No. 16 was the acidulated Carolina and Florida rock used in the above experiments. When treated with the separating solution, a small amount came to the top. There was, however, no trace of phosphoric acid in this portion. It took an hour for the solution to become clear, showing the presence of some substance, probably calcium sulphate and aluminum phosphates, of specific gravity but little higher than that of the solution, namely, 2.26.

The method of analysis were those of the Association of Official Agricultural Chemists.

SUMMARY.

The following method is proposed for separating the insoluble phosphoric acid in mixed fertilizers derived from bone, tankage or other organic matter, from that derived from mineral phosphates.

SOLUTIONS AND APPARATUS.

Separating Solution : Seventy-five grams of potassium iodide and 100 grams of mercuric iodide are dissolved in 350 cc. water and evaporated over a water-bath to a specific gravity of 2.26. This solution should be kept in a small flask arranged like a wash bottle.

Other solutions necessary to determine available and total phosphoric acid.

Separating Tube : Two tubes one and three-tenths cm. internal diameter, one seven cm. in length, closed at one end, the other twenty cm. long. These are connected by a piece of stout rubber tubing, so that the lower part or bucket, can be separated by a screw pinch-cock from the upper portion.

Extraction Tube : A tube two and five-tenths cm. internal

diameter, slightly contracted at one end, which has a rim over which filter paper and cheese cloth can be tied.

Other apparatus as for available and total phosphoric acid determinations.

Manipulation : Two grams of the substance to be examined are transferred to the extraction tube and washed with from 100 to 225 cc. of hot water, depending upon whether or not water soluble phosphoric acid is to be determined. Dry thoroughly, remove substance carefully, using spatula, brush, and rubber tipped glass rod, and transfer to a separating tube. Add fifteen to twenty cc. of the separating solution, shake thoroughly and wash down the sides of the tube with a jet of the solution. After standing five minutes tap the lower part or bucket smartly with the finger, to release any light portion carried down with the heavy, and stir up the matter on top with a jet of solution.

Let stand until the solution is clear, or for one hour, clamp the rubber tube, place a beaker under the bucket, which is carefully removed, the fingers being encased in rubber finger tips. Filter the solution back into the supply flask, wash thoroughly, saving the first washings for evaporation to a specific gravity of 2.26 again, and treat for insoluble phosphoric acid in the usual way. The light portion is treated in a similar manner. If desired, the heavy and light portions can be treated as for total phosphoric acid, thus determining all of the phosphoric acid derived from inorganic and organic sources respectively, except the water soluble.

MIDDLETOWN, CONN.

SOURCES OF ERROR IN VOLHARD'S AND SIMILAR METHODS OF DETERMINING MANGANESE IN STEEL.[1]

BY GEORGE AUCHY.

Received April 16, 1896.

VOLHARD'S method of determining manganese is generally considered a very accurate one ; nevertheless, that the

[1] In this Journal, 18, 406, I omitted to state a precaution used in the manner of performing Drown's sulphur method there described. The solution from the Troilius' bulb is heated to boiling (preferably with the previous addition of permanganate solution) before filtering into it the hydrochloric acid solution from the graphitic residue. This is to oxidize any sulphur that may be present as sodium sulphide.

accuracy of the process is strictly dependent upon certain conditions and precautions not pointed out by the author, and not generally recognized (so far as the writer is aware) seems proved by the experience with the method and with Stone's modification of it, which follows :

STONE'S MODIFICATION.

Mr. Geo. C. Stone makes a very considerable saving in time by omitting the evaporation with sulphuric acid, and precipitating the iron immediately with zinc oxid as soon as solution of the drillings in nitric acid is effected.[1] But in Volhard's original article, as also in Blair's Chemical Analysis of Iron, it is directed to destroy the carbonaceous matter by evaporation to dryness and strongly heating, or by evaporation with sulphuric acid till fumes of the latter come off, and as previous to the appearance of Mr. Stone's paper the writer, on testing this point by dissolving in sulphuric acid with enough nitric added to oxidize the iron and help effect the solution of the drillings and omitting the evaporation, had obtained results several hundredths higher (although Volhard's objection to organic matter is that it hinders the balling together of the manganese dioxide in titration) than those obtained from the same samples by the regular process, it was judged that this precaution was not a useless one ; and after reading Mr. Stone's article it was therefore considered well, as a precaution, to test his process also in this particular, and for that purpose the following determinations were made :

TABLE I.

No.	Carbon. Per cent.	Volhard's method. Per cent.	Stone's modification. Per cent.
476	0.585	0.46	0.53
495	0.80	0.57	0.65
503	0.228	0.423	0.45
505	0.225	0.49	0.52
483	0.17	0.43	0.51
486	0.185	0.54	0.61
507	0.315	0.44	0.44

[1] This Journal, 18, 228. Mr. Stone finds that hydrochloric acid solution also works well.

The results of Stone's method were very considerably higher than those by the regular method, except in the case of 507. But in the case of 507 it was noted that in making the precipitation of the iron by the zinc oxide a large excess had been accidentally used, while in all the other determinations the zinc oxide had been added in amount sufficient to precipitate the iron merely; and it was therefore thought advisable to see whether the considerable differences in the results by the two method's—Volhard's and Stone's—was not due to this fact (insufficient neutralization in the latter) before attributing it to the organic matter undestroyed in Stone's method. The above determinations were therefore repeated, using in each case not only enough zinc oxide to coagulate the solution and precipitate the iron as directed, but also enough in excess of this amount to turn the brownish red color of the iron precipitate to a light brown. The results follow:

TABLE II.

No.	Carbon. Per cent.	Volhard. Per cent.	Stone. Zinc oxide to coagulation. Per cent.	Stone. Zinc oxide in large excess. Per cent.
503	0.228	0.423	0.45	0.45
505	0.225	0.49	0.52	0.51
483	0.17	0.43	0.51	0.45
483	0.17	0.43	0.51	0.45
486	0.185	0.55	0.61	0.58
486	0.185	0.54	0.61	0.58
476	0.585	0.46	0.53	0.47
495	0.80	0.57	0.65	0.60
471	0.105	0.38	....	0.40
480	0.10	0.35	....	0.36
493	0.57	0.46	....	0.47
507	0.315	0.435	....	0.44
153	0.50	0.64	....	0.70
153	0.50	0.64	....	0.67
153	0.50	0.64	....	0.69
155	0.40	0.56	....	0.56

These results show that when the zinc oxide is added merely to coagulation and precipitation of the iron, leaving the solution probably faintly acid, the manganese is afterward precipitated, not according to the theoretical formula, but with result too high;

and that to insure the correct precipitation of the manganese it is necessary to add the zinc oxide in large excess, so that the solution is thoroughly neutralized when titrated.

It will, however, be noted that with this precaution, observed results in the table are nevertheless a few hundredths per cent. higher than by Volhard's method.[1] Is this difference due to the undestroyed carbonaceous matter? It was thought probable, but to make sure, some of the tests were repeated with oxidation of the carbonaceous matter by addition of lead dioxide to the boiling nitric acid solution of the drillings (the excess destroyed by ferrous sulphate and the excess of the latter oxidized by continued boiling of the nitric acid solution).[2] These results should be lower if carbonaceous matter has any influence. They were not lower, as the following table shows, and hence it is indicated that carbonaceous matter does not interfere. It is true that in one case (483) the result obtained by oxidation of the carbonaceous matter is lower, but the reason for this will appear later on.

TABLE III.

No.	Carbon. Per cent.	Stone. With carbon not oxidized. Per cent.	Stone. With carbon oxidized. Per cent.
480	0.10	0.36	0.37
507	0.315	0.44	0.44
155	0.40	0.56	0.55
155	0.40	0.56	0.57
155	0.40	0.56	0.56
155	0.40	0.56	0.56
153	0.50	0.70	0.68
483	0.17	0.45	0.41

Since the slightly high results obtained by Stone's method, in Table II., are not due to the undestroyed carbonaceous matter, they must be due to the fact of titration in nitric acid solution. The following determinations of manganese in solutions containing no organic matter, and in which the amount of mangan-

[1] It was later seen that the accuracy of the regular Volhard process was also dependent upon certain conditions; and the results by this method, given in these two tables, are the corrected results obtained later by checking with the color method according to Table VI. So that in Tables I. and II. the comparison is really with the color method rather than with Volhard's method. As explained under Table VI., there was not enough left of the samples for gravimetric tests. For a comparison of Stone's method with the gravimetric see Table XI.

[2] The lead dioxide and the ferrous sulphate used were tested for manganese.

ese was known (made by taking definite amounts of standard permanganate solution) are confirmatory of this conclusion:

TABLE IV.

No.	Manganese taken. Per cent.	Manganese found. Per cent.	No.	Manganese taken. Per cent.	Manganese found. Per cent.
1	0.40	0.41	8	0.40	0.42
2	0.40	0.41	9	0.80	0.81
3	0.40	0.41	10	0.80	0.82
4	0.40	0.41	11	1.20	1.24
5	0.40	0.41	11	1.20	1.22
6	0.40	0.41	13	0.80	0.81
7	0.40	0.42	14	1.20	1.22

Here, then, is a second precaution to be observed in Stone's method: a correction of the result by one or two hundredths per cent. must in each case be made. But still other precautions are necessary, as will appear.

VOLHARD'S METHOD.

The fact brought out by working upon Stone's method, that titration in faintly acid (nitric) solution gives too high results led to the suspicion that the same was also true of Volhard's regular method (sulphuric acid solution). The following tests were made:

TABLE V.

No.	Volhard. Zinc oxide added to coagulation.	Volhard. Zinc oxide in large excess.
490	0.49	0.39
490	0.49	0.39
490	0.49	0.39
490	0.49	0.49
476	0.51	0.46
507	0.49	0.44
483	0.45	0.41
503	0.45	0.41
471	0.41	0.38
289	0.42	0.40
289	0.42	0.40
493	0.51	0.44
505	0.50	0.46
155	0.58	0.49
155	0.58	0.56
289	0.42	0.41
153	0.66	0.64

Results of the first column were obtained by adding zinc oxide till the solution stiffened and the iron all precipitated. In the second column of determinations the zinc oxide was added in sufficient excess of this amount to make the color of the precipitated iron a light brown. The differences in the results were supposed to be due to this fact already noted in considering Stone's method—that titration in slightly acid solutions gives too high results. But a suspicion arose that these differences might, in part at least, be due to manganese being mechanically carried down with the iron when the large excess of zinc oxide was used. The obvious test of this would have been to make gravimetric determinations in the samples used in the last table. But, unfortunately, there remained but very little drillings of each of the samples. So the next best thing was done, and a standard manganese sample was prepared, and the determinations of these samples of the last table made by the color method: in each case making a number of tests and taking the average. Results:

TABLE VI.

No.	Volhard. Zinc oxide to coagulation.	Volhard. Zinc oxide in large excess.	Color method.
490	0.49	0.39	0.48
507	0.49	0.44	0.435
483	0.45	0.41	0.43
503	0.45	0.41	0.423
471	0.41	0.38	0.38
289	0.42	0.40	0.40
492	0.51	0.44	0.46
503	0.50	0.46	0.49
155	0.58	0.49	0.56

Showing that when the neutralization with zinc oxide is carried only to the point of precipitating the iron the result will invariably be from 0.01 per cent. to 0.05 per cent. too high; while on the other hand, if the zinc oxide be added in excess of this amount, the result *may* be too low, and very much too low from the precipitation of manganese with the iron. These points would have been more certainly and satisfactorily proved, however, had the comparison of the Volhard results been made directly with results by the gravimetric process instead of by the

color test. In the following table such comparisons with the gravimetric method—in a new lot of steels—are made, and confirm the conclusions drawn from the preceding table. In the second column of tests, the neutralization was performed in a way not to precipitate the manganese. In the third column of tests, neutralization was purposely performed in a way most favorable to the precipitation of manganese with the iron.

TABLE VII.

No.	Zinc oxide to coagulation. Per cent.	Excess of zinc oxide. The excess added after filtration of ferric oxide. Per cent.	Excess of zinc oxide. Added suddenly to the iron solution. Per cent.	Gravimetric method. Per cent.	Color method. Per cent.
451	0.56	0.51	0.51	0.52 (acetate)	0.53
452	0.46	0.44	0.44	0.43 "	0.435
453	0.46	0.46	0.37	....	0.425
454	0.47	0.47	0.44	0.46 (Ford)	0.45
493	0.51	0.46	0.44	....	0.46
456	0.45	0.41	....	0.41 (Ford)	0.43
466	0.54	0.49	....	0.485 "	0.49
481	0.48	0.45	....	0.455 "	0.46
153	0.66	0.64	....	....	0.64
000	1.30	....	....	1.25[1]	....

Insufficient neutralization gives high results. Complete neutralization *suddenly*, gives low results. Here then is the explanation for the low result of Table III (483); the ferric oxide precipitate had carried down some of the manganese.

The remedy is obvious. It is to carefully avoid an excess of zinc oxide at the time of precipitating the iron; adding the necessary excess to the aliquot part of the filtrate from the ferric oxide, taken for titration—filtering off the undissolved zinc oxide before titrating. But this procedure involves considerable extra work. And it does not seem necessary, if certain precautions be taken, to filter off the ferric oxide before adding the excess of zinc oxide. For it is reasonable to suppose that it is the *sudden* addition of the zinc oxide in excess to the rather concentrated solution that carries down the manganese. If the iron be first precipitated carefully by the gradual addition of zinc oxide, avoiding an excess, we have seen that no manga-

[1] Made by Williams, of Boston.

nese is carried down. If now, the solution be diluted, mixed, and the ferric oxide be allowed time to begin to settle, there seems no reason why the further addition of an excess of zinc oxide should then precipitate manganese. That it does not is evidenced by the preceding table, second column of results, last four results, which were obtained in this way. Also all of the determinations by Stone's modification in Table XI.

In the determination of the results of the third column of results in the preceding table, pains were taken to add the excess of zinc oxide as suddenly as possible; nevertheless, only three out of the five results are low, showing (as also do the results of Table VI.) that manganese is not invariably carried down by such a procedure. In Stone's modification the tendency to a precipitation of manganese with the iron seems less; for of the numerous results by that method (obtained before the necessity of any precaution in precipitating the ferric oxide was known) only one is low. But in both methods the neglect of the precaution to *thoroughly* neutralize with zinc oxide almost invariably gives results more or less above the truth.

Taught suspicion by the experience thus far had, it was resolved to test every step in the method; and the following determinations were made to see if the temperature of the liquid at the time of neutralization with zinc oxide had any influence upon the result:

TABLE VIII.

Solution heated to boiling with the zinc oxide.			Zinc oxide to cold solution.		
No.	Manganese taken. Per cent.	Manganese found. Per cent.	No.	Manganese taken. Per cent.	Manganese found. Per cent.
1	0.40	0.49	1	0.40	0.40
2	0.40	0.44	2	0.40	0.40
3	0.40	0.43	3	0.40	0.40
4	0.40	0.47	4	0.40	0.40
5	0.40	0.42	5	0.40	0.40
6	0.40	0.41	6	0.40	0.39
Solution merely warm.			7	0.40	0.40
1	1.20	1.22	8	0.40	0.41
2	0.80	0.83	9	0.40	0.40
			10	0.80	0.80
			11	1.20	1.20

These results show that neutralization must be performed in the cold. The writer had always practiced this precaution, though for no well defined reason.

The second series of results in the table also show that there is no tendency to slightly high results, as is the case when titration is done in nitric acid solution (Stone's method).

Volhard, in his article, states that the precipitated manganese dioxide is mixed with protoxide unless some metallic base like zinc oxide, lime, magnesia, etc., be present; and, therefore, in the following experiments on this point it was expected that the results would be poor, since the amount of zinc oxide present was purposely kept as low as possible by making the neutralization first with sodium carbonate, and then cautiously adding sulphuric acid till slightly acid, the slight excess of acid being then neutralized with zinc oxide.

TABLE IX.

No.	Taken. Per cent.	Found. Per cent.	No.	Taken. Per cent.	Found. Per cent.
1	0.40	0.41	4	0.40	0.41
2	0.40	0.42	5	0.40	0.42
3	0.40	0.40			

These results seem to show that this is not a very important source of error. In Särnström's method the point is entirely disregarded.

Five determinations made with five cc. free sulphuric acid (two to one) at time of neutralization with zinc oxide give, instead of the theoretical 0.40 per cent. taken, respectively 0.40 per cent., 0.42 per cent., 0.41 per cent., 0.41 per cent., 0.41 per cent.

With six cc. free acid, 0.40 per cent., 0.41 per cent.

With eight cc. free acid, the results of Table VIII.

.. ..

SÄRNSTRÖM'S METHOD.

Messrs. Mixer and DuBois recommend this method for iron ores,[1] and give results showing its accuracy. In this method zinc oxide is not used, the neutralization (hydrochloric acid

[1] This Journal, **18**, 385.

solution) being effected entirely by sodium carbonate, with care not to add it in greater amount than necessary to precipitate the iron, and the subsequent titration is done without filtering off the ferric oxide thus precipitated. This manner of neutralization leaves the solution not thoroughly neutralized, and from the foregoing results of this article we should expect high results from Särnström's method. The results given by Messrs. Mixer and DuBois are, however, excellent results; and this indicates either that neutralization with sodium carbonate in hot hydrochloric acid solution is not attended with the same phenomena as neutralization with zinc oxide in nitric and sulphuric solutions, or that in the former process there is a greater tendency of the manganese to precipitate with the iron, and that the error from this source counterbalances the error from titrating in faintly acid and hot solution. But the uniform excellence of the results given by Messrs. Mixer and DuBois points to the former as the more likely supposition. The method was briefly tested by taking standard manganese solution. Instead of 0.40 per cent. manganese taken in one case, 0.44 per cent., and in another 0.38 per cent. was obtained. But the test was not a fair one as there was no iron present to give the exact point of neutralization as obtained in the regular working of this method. Ferric chloride should have been added, but none was at hand, and the writer postponed further examination of the method for the reason that (as explained by Messrs. Mixer and DuBois) it is not well adapted to the analysis of steel.

COLOR METHOD.

The color method has no kinship to Volhard's, and its consideration is therefore hardly relevant here. But, nevertheless, as it was found necessary in the course of this work to make determinations by this method for comparison with others obtained by Volhard's method in samples almost used up, it might perhaps be just as well to give these color results in detail, as showing the limits of error in the process when performed by one not an expert in its use.

TABLE X.

No.	First reading. Per cent.	Second reading at a higher dilution. Per cent.		Volhard or gravimetric method. Per cent.	
289	0.40	0.40	0.40	0.40	Volhard.
	0.395	0.39			
	0.40	....			
153	0.63	0.64	0.64	0.64	Volhard.
	0.61	....			
	0.639	0.65			
503	0.552	0.547	0.56	0.56	Stone.
	0.564	0.560			
	0.572	0.586			
	0.543	0.555			
503	0.43	....	0.423	0.41	Volhard.
	0.426	0.416			
	0.42	0.425			
	0.42	0.42			
505	0.495	0.49	0.49	0.49	Stone.
	0.49	0.48			
	0.485	0.485			
	0.495	0.495			
483	0.44	0.425	0.43		
	0.425	0.425			
486	0.53	0.534	0.54		
	0.54	0.546			
471	0.38	0.37	0.38	0.38	Stone.
	0.39	....			
490	0.48	0.48	0.48		
	0.48	0.486			
493	0.438	0.445	0.46	0.46	Volhard.
	0.47	0.466			
	0.468	0.47			
507	0.43	....	0.435	0.42	Stone.
	0.43	0.44			
466	0.488	0.472	0.49	0.485	Gravimetric.
	0.497	0.498			
481	0.49	0.475	0.469	0.455	Gravimetric.
	0.50	0.49			
	0.455	0.454			
	0.47	0.46			
	0.446	0.446			
	0.476	0.47			
453	0.43	0.426	0.425	0.425	Stone.
	0.416	0.425			
456	0.449	0.446	0.43	0.41	Gravimetric.
	0.427	....			
	0.417	0.42			
	0.416	0.428			
	0.417	0.414			
451	0.545	0.56	0.53	0.52	Gravimetrtc.
	0.53	0.53			
	0.54	0.54			
	0.52	0.52			
	0.52	0.525			
	0.537	0.545			
	0.535	0.531			

The results in the table by Volhard's and by Stone's method were obtained by an observance of precautions given—correction of 0.02 per cent. in results by the latter method, thorough neutralization by zinc oxide, etc.

It will be seen that color method results are quite accurate if a number of color comparisons be made and the average taken. But if only one test be made the variation may occasionally be 0.02 to 0.03 per cent. But in these determinations the boiling was all done over the naked flame. Closer results can perhaps be had by using the calcium chloride bath for this purpose, as directed in Blair's Chemical Analysis of Iron.

RECAPITULATION.

The sources of error, then, in Volhard's process, as indicated by the foregoing experiments, are :

1. The incomplete neutralization by zinc oxide, giving usually high results.

2. The too sudden addition of the necessary excess of zinc oxide, giving frequently low results.

3. The titration in nitric acid solution giving results 0.01 or 0.02 per cent. too high.

4. Neutralization by zinc oxide in hot solution, giving high results.

With regard to the first of these sources of error it may be remarked that Volhard recommends slightly acidifying with nitric acid before titration—to oxidize organic matter. But whatever organic matter may be present capable of being oxidized by nitric acid has already been oxidized, and the organic matter and proto salts present in the sodium carbonate and zinc oxide used for neutralization is best determined by a blank or dummy test, or better by performing the process with a convenient measured amount of standard permanganate decomposed by hydrochloric acid. Besides the error from titrating in faintly acid solution, a further objection to acidifying with nitric acid is that the manganese dioxide precipitated by titration collects as a film on the glass and obscures the end reaction.

Stone's modification is much easier and quicker than the regu-

lar Volhard method; not only because the evaporation to dryness with sulphuric acid is dispensed with, but also, as Mr. Stone points out, because in nitric acid solution the precipitated ferric oxide settles so readily and completely that the filtration from it may be omitted, the clear liquid being decanted from the precipitate. In sulphuric acid solution the precipitated ferric oxide does not settle readily enough for this, and thus considerable time is taken up in making folded filters, and the filter paper used adds appreciably to the expense of the method.

Mr. Stone performs the neutralization entirely with commercial zinc oxide, and this is doubtless the reason that his results have always been satisfactory, and he has noticed no necessity for the precaution of thorough neutralization; for in neutralizing altogether with zinc oxide, in the hurry of every day work one would naturally get a large or a considerable excess of it used, even if not recognizing the necessity for such an excess. And as to the precipitation of manganese with the iron, the work in this article would seem to show that to be an exceptional occurrence with nitric acid solution, although of frequent occurrence in sulphuric acid solution if caution be not used in the neutralization. But as regards neutralization, the writer considers it more advantageous to use sodium carbonate, or common sal soda first, finishing up with zinc oxide emulsion, for sal soda is much cheaper than commercial zinc oxide. But, as before mentioned, the manganese, organic matter, and proto salts in these reagents, if any be present, must be allowed for.

Mr. Stone takes 100 cc. for titration. But 250 cc. is perhaps preferable on the score of greater accuracy. The writer finds it convenient to use permanganate of strength exactly 0.0056, taking always three and three-tenths grams of the drillings for analysis. The reading of the scale on the burette then at once gives the percentages of manganese without calculation, except a division by ten.

For the convenience of those unfamiliar with the process details briefly follow, with the precautions found to be necessary in this article printed in italics. Three and three-tenths grams of drillings. Dissolve in fifty cc. nitric acid, sp. gr. 1.20. Wash

into a 500 cc. measuring flask. Add about two-thirds of the amount of sal soda solution necessary to a complete neutralization. *If not cold, cool.* Add zinc oxide emulsion till solution stiffens, *avoiding an excess.* Dilute to about three-fourths of the capacity of the flask, mix and let stand till the ferric oxide begins to settle. See that the solution is colorless. *Add considerable excess of zinc oxide emulsion.* Mix. Dilute to mark. Insert stopper. Mix. Transfer to dry beaker. Mix again. Let settle, and pour off 250 cc. Titrate in 500 cc. Erlenmeyer flask, (first heating to boiling) with permanganate of strength 0.0056. Make the necessary deduction for impurities in the sal soda and zinc oxide. Divide the number of cubic centimeters permanganate taken by ten. *Deduct 0.02 per cent.*

Following are some comparisons of results by this method with results by Volhard's method, gravimetric method, and color method:

TABLE XI.

No.	Volhard with all precautions. Per cent.	Stone with all precautions. Per cent.	Gravimetric. Per cent.	Color. Per cent.
1451	0.51	0.51	0.52	0.53
452	0.44	0.42	0.43	0.435
453	0.46	{ 0.42 { 0.43	....	0.425
453	0.47	0.45	0.46	0.45
493	0.46	0.47	....	0.46
466	0.41	0.41	0.41	0.43
466	0.49	0.49	0.485	0.49
481	0.45	0.46	0.455	0.469
153	0.64	0.65	....	0.64

A SIMPLE FORM OF GAS REGULATOR.[1]

BY LUDWIG SAARBACH.

Received April 17, 1896.

A GLASS tube, one end of which is blown out to a bulb is bent around twice, as indicated in Fig. 1, and is provided with a side tube *T*. Some mercury is poured into it, which cuts off a volume of air in bulb *A*. The smaller tube *I* fitting loosely in the wider tube, is connected with the latter by a piece of rubber tubing, which at the same time allows an up and down

[1] Read before the New York Section, April 10th, 1896.

movement of the small tube. This apparatus is put into the air or water bath, which is to be kept at a constant temperature; its working is effected by the expansion by heat of the

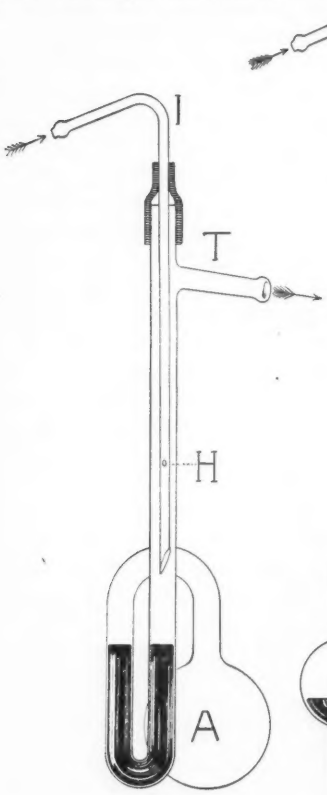


Fig. 1.

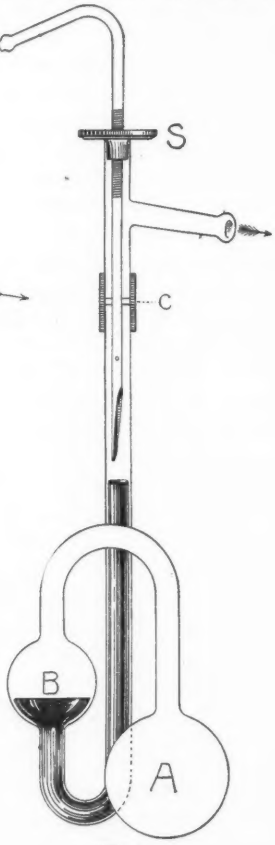


Fig. 2.

volume of air in bulb *A*, which causes the mercury column to rise until it reaches pipe *I*, serving as inlet of the gas. From the space over the mercury column, the gas is conducted through the pipe *T* to the burner. As the inlet pipe is cut off

obliquely or drawn out to a slit, the supply of gas is with increased temperature diminished by and by, and might even be cut off altogether if the pipe were not provided with a small hole *H*, which allows the passage of a sufficient amount of gas to prevent the extinction of the flame. The smaller supply of gas lowers the temperature, and the sinking of the column of mercury caused thereby allows then the gas to pass again freely. It is easy to keep the air- or water-bath, which is provided with this apparatus, constantly at any desired temperature within 1° to 2° F. by regulating the position of the inlet pipe. The daily changes in the atmospheric pressure have very slight influence.

As the amount of mercury might at higher temperature not be sufficient to keep back the expanded air a small bulb might be blown in the second bend (B, Fig. 2), and thereby a sufficient supply of mercury for even very high temperatures can be provided. If the apparatus is intended for a closed bath, the main pipe is cut at *C*, the lower part is then fixed from inside and connected outside with the upper part by means of rubber tube. The standpipe *l* may also be regulated by a screw movement *S*.

This apparatus has the advantage of being simple and cheap. It can be used for open or closed baths at either high or low temperatures. The main drawback of all other similar apparatus is the black mass caused by the action of illuminating gas on the mercury, which collects in a short while on the surface of the mercury column and stops the action completely. The apparatus described allows the removal of the dirty mercury and filling anew in the easiest and most rapid manner.

Furthermore, there is no stop-cock or rubber tube connection between the working parts, that is, the expanded volume of air and the column of mercury.

A RAPID METHOD OF DETERMINING THE MOLECULAR MASSES OF LIQUIDS BY MEANS OF THEIR SURFACE TENSIONS.

By C. E. Linebarger.

Received May 13, 1896.

INTRODUCTORY.

UNTIL within the last few years our knowledge of the molecular condition of liquids was very limited. Such facts as the existence of allotropic modifications of elements and of isomorphous forms of compounds, the rotation of the plane of polarized light, the abnormal vapor-densities of certain substances in the vicinities of their boiling points seemed to indicate that in liquids two or more gaseous molecules coalesce to form complex molecular groupings.[1] Indeed, de Heen[2] developed a theory of liquids on the hypothesis that liquid molecules are made up of a number of gaseous molecules, thus making a distinction between "liquidogenic" and "gasogenic" molecules. On the other hand, it has been assumed by some that the differences between gases and liquids are due solely to the greater propinquity of the molecules in the liquid condition, no polymerization of the gaseous molecules taking place. But nothing really definite about the question was advanced until Guye,[3] in studying the relation of his critical coefficient to the molecular mass of a liquid at its critical point, found that it was necessary to double the molecular masses of methyl alcohol and water in order to make them conform to the general rule he had established. This is the first time that a definite numerical value was assigned to the molecular mass of a liquid, and it was thereby rendered evident that both of the above suppositions in regard to the molecular condition of liquids correspond to fact; some liquids are polymerized and some are not.

[1] Naumann: *Ann. Chem.* (*Liebig*), **155**, 325, *1870*; Henry: *Ann. de la Soc. Scientifique de Bruxelles*, *1878-1879*, 267; Spring: *Bull. del'Acad. de Belgique* [3], **11**, No. 5, *1886*; Dupré: Théorie mécanique de la chaleur, 147; Amagat: *Ann. chim. phys.* [5], **11**, 536; Ramsay: *Proc. Roy. Soc.*, *1880*, April 22 and December 16; Ramsay and Young: *Proc. Roy. Soc.*, *1885*, Nov. 19, and *Phil. Mag.*, *1887*, 129.

[2] de Heen: *Ann. chim. phys.* [6], **5**, May, *1885*, and Physique Comparée et la Theorie de Liquides, *1888*.

[3] *Ann. chim. phys.* [6], **21**, Oct. *1890*; *Compt. rend.*, **110**, 141 and 1128, *1890*; *Bull. Soc. Chim.* [3], **3**, 51; Arch. de Genève. [3], **23**, 197; Thesis: Le coefficient critique et la determination du poids moleculaire au point critique. Paris, *1891*.

The next stage in the investigation of the subject was naturally the determination of the classes of liquids that are made up of simple molecules and of the classes of liquids that consist of complex molecules, or, in other words, the determination of which liquids are "normal" and which are "associated;" also the question as to the amount of association presented itself.

This investigation was taken up by Ramsay and Shields,[1] who, by the application of a method based upon determinations of surface energies, examined more than fifty liquids; this work may justly be considered classic and is the source of most of our definite knowledge of the size of liquid molecules.

The division of liquids into two classes according to their molecular polymerization having thus been rendered familiar and definite by the work of these two English chemists, many properties of liquids were subjected to examination in order to ascertain whether they might reveal any indications of molecular polymerization. Guye[2] has been particularly active in this direction; thus, he found evidence of molecular association in certain liquids, as shown by their latent heats of vaporization attaining a maximum, their curves of vapor-tensions intersecting one another, etc. Also, Linebarger,[3] in examining Pictet's Law (commonly but erroneously known as Trouton's Law) and in determining the specific gravities, viscosities, and other physical properties of mixtures of liquids found that certain abnormalities could be best accounted for by the assumption of the presence of polymerized molecules. Moreover, in studying the vapor-tensions of mixtures of volatile liquids, Linebarger[4] was led to the discovery of a method of determining the absolute molecular mass of a liquid at a definite temperature, Ramsay and Shield's method giving only the average molecular mass throughout a certain range of temperature.

Mention must also be made of an extremely simple method proposed by Traube[5] for ascertaining whether the molecules of a liquid are in a state of association or not; it is based upon a

[1] *J. Chem. Soc.*, **63**, 1089, *1893*, and *Ztschr. phys. chem.*, **12**, 433, *1893*.
[2] Arch. de Genève [3], Jan., Feb., and May, *1895*; *Bull. Soc. Chim.*, **13**, **34**, *1895*.
[3] *Am. J. Sci.*, **49**, 381, *1895*; *Am. Chem. J.*, **18**, 429.
[4] *J. Am. Chem. Soc.*, **17**, 615 and 690, *1895*.
[5] *Ber. d. chem. Ges.*, *1894–1896*.

determination of the density of the liquid under investigation.

The discovery of a method of determining the molecular masses of liquids opens up a broad field of investigation. The discoverer of a new liquid ought no longer to be content with a determination of its vapor-density or cryoscopic behavior in order to ascertain its molecular mass in the gaseous or dissolved state; he ought also to determine its surface tension, its density, or its vapor-tension in solution in order to ascertain whether it is associated or not. The method of vapor-tensions in solution, although it is the only one as yet devised that gives indications of the exact size of a liquid molecule at a given temperature, is rather long and is restricted to volatile liquids capable of analysis in the presence of the solvent. The chemist is therefore confined to the methods by Ramsay and Shields, or Traube. As stated above, Traube's method depends simply upon a determination of density; it does not seem to have attracted much attention, probably because it has merely an empirical basis. But a density determination is also required in Ramsay and Shields' method, so that the two methods may be employed together, the one serving as a control of the other.

The method of determination of molecular masses of liquids from their surface energies, as carried out with the apparatus used by Ramsay and Shields, does not seem to have been generally introduced into laboratories of organic chemistry for the probable reason that it requires careful and skillful manipulation and considerable time. There appears to be a need for an apparatus that can be handled rapidly, does not require much skill in using, is always ready for work, and gives reliable results. It is believed that the apparatus to be described in the following sections meets these requirements.

II. DESCRIPTION OF APPARATUS.

The apparatus (Fig. 1) consists of the following pieces: A column of brass tubing *AA* with iron tripod base; a short horizontal arm *B*, to which is attached a brass gibbed plate *SS* supporting the capillary tubes by means of the clamps *CC* and *DD*, and also the micrometer screw *EF*; a retort ring *AH* bearing the beaker *II*; a compression device consisting of a screw *L*

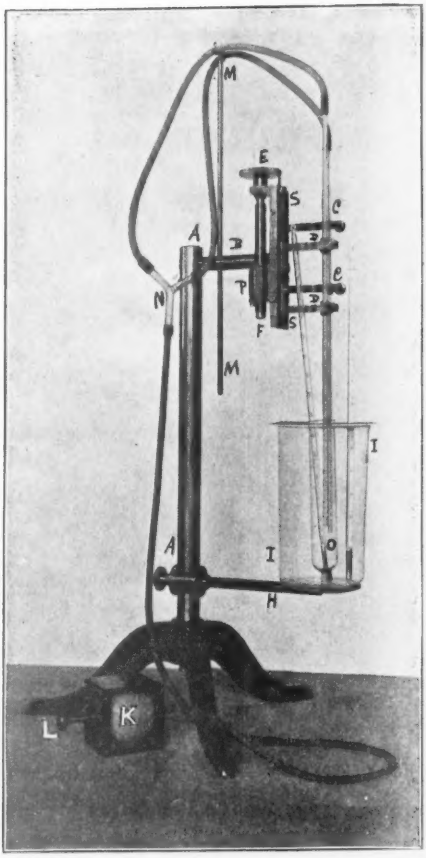


Fig. 1. Apparatus for Determining the Surface Tensions of Liquids. (*To Face p. 516.*)

pressing into a rubber ball K, which is connected by means of rubber tubing and a glass Y tube N to the upper extremities of the capillary tubes; a vertical rod MM passing through the arm B (to which it may be clamped by a thumb-screw not shown in the figure) and provided with rings to support the rubber tubes connected with the capillary tubes, the latter being thus relieved of the weight of the former; a test tube O, into which the capillary tubes pass, supported by the cover of the beaker H; two thermometers, one to take the temperature of the bath-liquid contained in the beaker, the other that of the liquid undergoing investigation in the test tube O.

Some of these pieces require a more detailed description.

The immovable part of the gibbed plate has a scale fastened along its side divided into fortieths of an inch, while its movable part has a pointer playing over this scale. Back of the gibbed plate is fixed the bearing P, in which the screw EF turns; the clamps CC are attached to the fixed portion of the gibbed plate, also another pointer for the milled head of the screw.

The micrometer screw demands a specially detailed description, inasmuch as the accuracy of the results obtainable by the apparatus depend mainly upon the accuracy of its construction. The one I use has forty threads to the inch, is about four inches long, and of good diameter, so as to give absolute motion, the adjustable split bearing P taking up all lost motion. Great pains were taken in turning it, and I have been unable to detect any irregularities in its construction; indeed, the screw furnished by the makers is even more accurate than is really necessary. The milled head E (about thirty-five mm. in diameter) is divided into 100 parts, thus giving a direct reading of $\frac{1}{4000}$ of an inch, and even less than that, since it is easy to estimate fractions of a division.

Three capillary tubes were employed in working with the apparatus:

A with a bore of about one and a half mm.
B " " " " " five-tenths mm.
C " " " " " one-tenth mm.

From the nature of the method it is not at all necessary to know the exact dimensions of the tubes; all that is required is

that the bore be approximately circular and the edges sharp. To prepare the capillary tubes, a stock of tubing is examined and tubes of the desired dimensions selected. Pieces are broken off from these tubes until it is found that the ends present plane surfaces perpendicular to the axis of the tube. If the clamps happen to be too large for the tubes, a filling of sheet lead may be employed.

The liquid serving as bath and contained in the beaker may be water or glycerin; it is heated by means of a Bunsen burner and kept in motion by means of a stirrer (not shown, however, in the figure). Besides this kind of a bath much use was made of a vapor jacket for keeping the temperature uniform during a determination. The test tube *O* was fitted into a considerably larger tube by means of a cork, through a second perforation of which passed a long glass tube acting as a condenser. On boiling liquids or mixtures of liquids in the larger tube, their vapors rise and heat the inner tube with its contents to a desired constant temperature for any length of time.

III.—METHOD OF MAKING A DETERMINATION.

The first thing to do in using the apparatus is to get the lower extremities of the two capillary tubes at the same level. This may be accomplished in the following simple manner. A spirit-level is placed upon a piece of plate glass, which in turn is set upon the support *H* at the required height and levelled. The pointers of the side scale, as well as that of the screw head, are set at zero, the tubes allowed to rest freely upon the plate glass, and then clamped into position. While this way of fixing the tubes answers well enough for the initial adjustment of the apparatus, it is not sufficiently accurate to insure their being replaced in the same position, if, from any cause, they become displaced. Indeed, it is not at all certain that the tubes are at the same level to within 0.1 mm., when adjusted in the above manner; yet this degree of accuracy is entirely sufficient for the first adjustment, and later it will be shown how they can be gotten into the same position to within 0.01 mm.

The test tube has a mark scratched on its side, which indicates the volume of liquid that is to be taken for a determination

of its capillary constant, it having been found that differences in the distance between the surface of the liquid and the orifices of the tubes have a little influence upon the readings of the instrument.[1] The volume of the liquid may be as small as a couple of cubic centimeters, if a small test tube be used; generally, however, it is advisable to employ from five to ten cc. The test tube is filled with the liquid under examination to this mark and the tube suspended in the bath. The beaker is placed upon a piece of asbestos board or wire gauze set upon the retort ring, which is raised until the capillary tubes are close to the bottom of the test tube. A thermometer is introduced into the liquid, and the bath liquid stirred so as to insure uniformity of temperature.[2] The rapidity with which the liquid undergoing investigation takes on the temperature of the bath may be hastened by blowing bubbles up through it by compression of the air in the rubber ball *K*.

When the temperature of the liquid is the same as that of the bath, the movable tube (preferably the one with the smaller bore), is raised by turning the screw. This may be done rapidly while bubbles are being forced out of the larger tubes every second or so. At a certain point bubbles may cease to issue from the larger tube and commence to come from the smaller one, an indication that the correct adjustment has been passed. The screw is now turned very cautiously in the opposite direction until bubbles issue at about the same time from both of the tubes. The final adjustment is generally best made as follows:

The air is compressed *very slowly* until it has arrived just at the orifices of both tubes. The pressure is then not increased further, and, as a rule, it will be observed that, if the adjustment is perfect, bubbles will issue of their own accord from both the tubes in a second or so; sometimes one of the bubbles lags a little behind the other. The success of the operation depends upon the *steady* and *gradual* compression of the air; if this be subjected to abrupt or irregular changes of pressure, not inconsiderable errors may be committed. It is advisable to make at

[1] This influence is, however, but slight. Readings with ether were found to differ by only $\frac{1}{100}$ of an inch, when the difference between the free surface of the liquid and the lower extremities of the capillary tubes differed by more than four inches.

[2] The mode of procedure is essentially the same when a vapor jacket is employed.

least two readings, one when the narrower tube is being lowered, the other when it is being raised; indeed, the readings can be made so rapidly that it is a good plan to take a half dozen or so, the tubes being moved alternately up and down.

IV.—DISCUSSION OF SOURCES OF ERROR IN APPARATUS.

In the determination of the capillary constants by means of the apparatus described in the preceding sections, measurements of three kinds have to be made, *viz.*, measurements of specific gravity, of temperature, and of the distance between the lower extremities of the capillary tubes. We pass to the discussion of the errors inherent to each.

I. The determination of the surface tensions by any of the direct methods, such as measuring the height to which liquids rise in capillary tubes, etc., cannot be said on an average to be accurate to more than one part in two thousand, and only in exceptional cases to one part in ten thousand. On the other hand the accuracy of a specific gravity determination can easily attain one part in ten thousand, and in many cases to even one part in a hundred thousand. In the formula to be communicated in the following section, it will be seen that the influence of the specific gravity upon the value of the capillary constant is not very great, so that a determination of the specific gravity to one part in two thousand is perhaps sufficiently accurate for our purposes, although it is of course better to be sure of the fourth decimal place. We may conclude then that the accuracy of a determination of the specific gravity of a liquid where surface tension is to be ascertained, may be counted perfect, if it be made to within one part in ten thousand.

II. For temperatures between 0° and 50° it is an easy matter to keep the temperature of even such a simple bath as the one given in Fig. 1 constant to within 0.05° long enough to adjust the apparatus and make several readings. By the use of the larger baths, or, better still, of vapor jackets, the temperature can be kept sufficiently uniform for the investigation at different temperatures of most liquids. As a variation of temperature amounting to 0.1° changes but little the readings of the apparatus, it may be allowed that the error committed in estimating the temperature is, for the purpose of this investigation, negligible.

III. The possible error that may be committed in the readings of the apparatus can best be judged by considering the readings themselves. A number of series of readings for different liquids at various temperatures are accordingly given just as they were taken directly from the apparatus.

The readings are not to be taken as material for the calculation of the surface tensions of the liquids, as in some cases they do not represent the true distances between the lower extremities of the capillary tubes, the positions of these having been altered purposely several times. The unit of a reading is a fortieth of an inch.

Nitroethane[1] at 16.95°. Tubes A and B.	Nitroethane[1] at 46.6°. Tubes A and B.
23.27	21.23
23.26	21.26
23.28	21.21
Nitromethane[1] at 24.5°. Tubes A and B.	**Nitromethane[1] at 41.5°. Tubes A and B.**
24.28	22.86
24.26	22.87
24.23	22.80
24.25	22.81
24.29	22.85
24.26	
24.26	
Benzene at 20.0°. Tubes A and B.	**Benzene at 20.5°. Tubes B and C.**
22.86	30.55
22.88	30.54
22.85	30.59
22.86	30.56
22.87	30.55
Toluene at 25.0°. Tubes A and B.	**Toluene at 46.6°. Tubes A and B.**
24.42	22.65
24.44	22.63
24.41	22.62
24.40	22.63
24.43	22.64
Another series made ten days later.	22.64
24.43	22.66
24.45	22.64
24.42	
24.43	
24.45	

[1] Made by Mr. L. W. Jones, of the University of Chicago.

Methyl nitrate at 0.2°. Tubes A and B.	Carbon bisulphide at 19.5°. Tubes A and B.
18.29	19.35
18.28	19.32
18.25	19.30
18.26	19.33
18.28	19.34
Ethyl ether at 0.1°. Tubes A and B.	**Ethyl ether at 25.0°. Tubes A and B.**
17.90	13.55
17.92	13.53
17.92	13.52
17.95	13.54
17.93	Another series made over a month later.
	13.54
	13.55
	13.53
Toluene at 78.4°. Tubes B and C.	**Monochlorbenzene at 77.8°. Tubes B and C**
24.73	23.34
24.77	23.38
24.75	23.32
24.71	23.35
24.74	23.34
Ethyl iodide at 25.0°. Tubes A and B.	**Ethyl alcohol at 51.0°. Tubes A and B.**
8.89	18.65
8.87	18.62
8.88	18.64
8.88	18.61
8.87	18.63
Another series made twenty days later.	
8.87	
8.86	
8.88	
Water at 40.0°. Tubes A and B.	**Water at 20.0°. Tubes A and B.**
77.10	76.09
77.13	76.13
77.14	76.10
77.09	76.16
77.11	76.23
77.16	76.14
77.13	76.16
77.12	76.18
	76.15
	Another series made a fortnight later.
	76.12
	76.18
	76.21
	76.19
	76.14
	76.18

These series of numbers have been taken from my note books almost at random, and are but a small portion of the number of readings I have made. They show that for most liquids differences in the readings amounting to more than $\frac{5}{4000}$ of an inch seldom occur, and when a series of readings are made and their average taken, the error almost vanishes. Only in case of water were greater differences of readings observed; yet, since water has such a large capillary constant, the error committed is very slight. It was observed that the nearer the extremities of the capillary tubes were, and, consequently, the smaller the numerical value of the reading, the more concordant were the readings.

While the three sources of error just discussed seem to be almost negligible, there is another, inherent, not in the apparatus, but in the method, which stands seriously in the way of obtaining reliable absolute determinations of the surface tensions of liquids. This source of error lies in the determination of the "apparatus constant," which may vary from one liquid to another. A more detailed discussion of it will be given in the next section, after the way in which the "apparatus constant" is determined is described.

V.—CALCULATION OF RESULTS.

Having now shown the degree of accuracy attainable in the readings of the apparatus under discussion, I will pass to the considération of the manner in which the results obtained by this indirect method may be converted into those arrived at by direct methods. As stated above, two things besides the temperature are measured in this method: (1) the specific gravity of the liquids taken, and (2) the vertical distance between the lower ends of the two capillary tubes when air under the same pressure issues in synchronous bubbles from their orifices. It is not difficult to determine the specific gravity to within $\frac{1}{50000}$, although an accuracy of $\frac{1}{10000}$ is quite sufficient. The distance between the ends of the two tubes can be measured to about a hundredth of a millimeter, except in the case of water, where the degree of accuracy of measurement is only within a tenths of the same unit of length. It is now our task to pass from the data obtained from measurements of these quantities to the capillary constants measured in dynes per centimeter.

Inasmuch as our knowledge of the form of the bubbles just on the point of issuing from the orifices of the capillary tubes is not at all precise, there appears to be no immediate way of finding a relation on theoretical grounds between the data furnished by this indirect method and those given by direct methods. Jäger[1] obtained the relationship employed by him in the following manner: "Wie sich unsere Annahme für die Formulirung des Einflusses, welchen die Röhrenweite auf den bewussten capillaren Druck hat, als richtig erwies, so zeigt sich, wie wir später sehen werden, dass es vollständig genügt, wenn wir

$$\alpha F(s) = \alpha(1 + \beta s)^2$$

setzen, wobei β eine Constante bedeutet, die sich ebenfalls leicht ermitteln lässt, wenn zwei Flüssigkeiten, deren α und s bekannt sind, zu Gebote stehen. Verwenden wir nämlich zu unseren Messungen stets dieselben beiden Capillarröhren, so wird für die eine Flüssigkeit die Gleichung (1)

$$\alpha(1 + \beta s)\varphi(r,r') = hs,$$

für die zweite,

$$\alpha'(1 + \beta s')\varphi(r,r') = h's',$$

somit

$$\frac{\alpha(1 + \beta s)}{\alpha'(1 + \beta s')} = \frac{hs}{h's'}.$$

Aus dieser Gleichung kann der Werth von β ermittelt werden da alle übrigen in ihr vorkommenden Grössen bekannt sind."

In order to obtain the value of β, he made use of Brauner's[3] and Wolf's[4] directly determined data for water and ethyl ether. By transforming the immediately preceding equation into

$$\alpha = \frac{\alpha' hs(1 + \beta s')}{h's'(1 + \beta s)},$$

he obtained therefrom on putting

$$\frac{\alpha'(1 + \beta s')}{h's'} = c,$$

$$\alpha = c\,\frac{hs}{1 + \beta s};$$

[1] *Loc. cit.*

[2] a = capillary constant; s = specific gravity.

[3] *Ann. der Phys. Pogg.*, 70, 515.

[4] *Ann. der Phys. Pogg.*, 70, 575.

and substituting for specific gravity $= s$, the specific volume $= v = \frac{1}{s}$, he finally obtained

$$\alpha = c \frac{h}{v + \beta},$$

an equation used throughout his work in transforming his results.

It is hardly necessary to mention that the degree of accuracy that can be attributed to an indirect method of measuring a physical constant of Nature depends upon the accuracy of the results obtained by direct methods; hence the importance of choosing the most exact directly determined data for the calibration of an indirect method. Ramsay and Shields[1] have elaborated the method of measuring the heights to which liquids rise in capillary tubes, and have carried out series of determinations of the capillary constants of various liquids in contact only with their own vapor and glass, which are justly regarded as of the greatest trustworthiness, and may be confidently taken as standards.

If Jägers equation,

$$\frac{\alpha(1 + \beta s)}{\alpha'(1 + \beta s')} = \frac{hs}{h's'},$$

be correct, it ought to be possible to obtain the same value of β, when the data for α and α', s and s', and h and h' are taken for any pair of liquids. On carrying out the calculations, however, I found, on employing the data given by Ramsay and Shields,[2] for the specific gravities and capillary constants, and the readings of my apparatus for the differences of level between the extremities of the two capillary tubes, that the values of β varied considerably for different pairs of liquids. Furthermore, it was found that, if β and c be calculated for any two liquids, and then from the equation

$$\alpha = c \frac{hs}{1 + \beta s},$$

the value of α be deduced for a third liquid, differences between the values thus obtained and those given by Ramsay and Shields amounting to five or ten per cent. were obtained in some cases,

[1] *Ztschr. phys. Chem.*, 12, 433, *1893*.
[2] *Loc. cit.*

although once in a while a pretty good correspondence was observed. Jäger's equation appears to be merely approximate and does not stand a rigid scrutiny. Jäger himself seems to find the justification of his formula in its yielding results corroborative of certain theoretical views he advances, and in the agreement between his observed values and those calculated for the same temperatures, by means of temperature coefficients; but as the temperature coefficients were derived from his own data, which differ but rarely more than five or ten per cent. from those communicated by Ramsay and Shields,[1] and he does not attain to a much closer correspondence than that between his observed and calculated values, the correctness of the formula does not seem to be any the better established.

It accordingly became peremptory to devise another formula which should be in better accordance with Ramsay and Shields'[2] measurements. But here a difficulty arose. Ramsay and Shields determined the capillary constants of liquids that had been freed from air; the liquids were in contact only with their own vapor and glass. There is no doubt but that the surface tensions of liquids can be measured accurately by means of their rise in capillary tubes only when no air is present; R. Schiff[3] had already made this observation before Ramsay and Shields. Just what influence the presence of air has upon the capillarity of liquids we do not know; the greater or less volatility of a liquid makes the degree of dilution of air in contact with its surface correspondingly greater or less. In the apparatus described in this article, the liquid under examination is saturated with air, and the pressure of the air varies with the specific gravity of the liquid. The difficulty at issue lies in the question as to whether the indirect determinations made with liquids in contact with air are comparable to more than a gross approximation with those obtained by the direct method as employed by Ramsay and Shields. This difficulty seemed at first to be unsurmountable, but, finally, a simple relation was discovered which shows an excellent correspondence between Ramsay and Shields' data and mine.

[1] *Loc. cit.*
[2] *Loc. cit.*
[3] Ann. Chem. (Liebig), 233, 47.

The relation in question is

$$\gamma = chs + s^3 \ldots\ldots\ldots (A)$$

wherein γ represents the capillary constant in dynes per centimeter, c the "apparatus constant," h the distance between the ends of the tubes, and s the specific gravity. The value of the constant was obtained in the following way. The data for γ and s were taken from Ramsay and Shields' and Ramsay and Aston's papers, and those for h from my own measurements. These were set in equation (A) and the value of c calculated therefrom. The greatest pains were taken in the purification of the liquids examined, so that they had no doubt the same properties as those used by the investigators just named. The data and results of the calculations are given in Table I. for the tubes A and B, and in Table II. for tubes B and C.

TABLE I.

Values of "Apparatus Constant" for Tubes A and B.

Name of liquids.	T.	s.	γ.	h.	c.
Water	20.0°	0.9984	70.72	55.60	1.248
"	30.0°	0.9958	69.10	54.85	1.247
"	40.0°	0.9923	67.50	53.90	1.245
Methyl alcohol...	20.0°	0.7905	23.03	23.16	1.227
Ethyl " ...	20.0°	0.7900	22.03	21.97	1.236
Acetone	16.8°	0.7798	23.35	22.95	1.238
"	46.4°	0.7656	19.68	20.00	1.250
Ethyl ether.....	20.0°	0.7143	16.49	17.91	1.245
" "	30.0°	0.7000	15.27	16.87	1.252
Ethyl iodide.....	19.1°	1.937	30.00	10.88	1.248
Carbon bisulphide	9.7°	1.2773	32.73	19.90	1.224
Benzene.....	11.2°	0.8871	29.21	25.86	1.239
"	46.0°	0.8500	24.71	22.75	1.241
Chlorbenzene.....	9.5°	1.1182	33.71	23.46	1.238
"	45.6°	1.0795	29.30	21.25	1.227
Toluene	15.2°	0.8682	28.18	25.21	1.253
"	46.6°	0.8380	24.60	22.65	1.259

Average = 1.243

TABLE II.

Values of "Apparatus Constant" for Tubes B and C.

Names of liquids.	T.	s.	γ.	h.	c.
Acetone	16.8°	0.7998	23.25	27.72	1.023
"	46.4°	0.7656	19.68	24.22	1.029
Chlorbenzene.....	45.6°	1.0795	29.30	25.71	1.014
"	77.8°	1.0444	24.65	23.38	1.011
Ethyl ether	20.0°	0.7143	16.49	22.08	1.036
Benzene	11.2°	0.8871	29.21	31.44	1.019
"	46.0°	0.8500	24.71	27.86	1.013
Toluene	15.2°	0.8682	28.18	30.60	1.032
"	46.6°	0.8380	24.60	27.75	1.028
"	78.4°	0.8080	20.93	24.75	1.014
					Average = 1.022

A glance at the tables shows that the "constants" are indeed quite constant. In Table I., the average of the numbers in the last column is 1.243; the greatest variation on one side is 0.019 for carbon bisulphide at 9.7°, and on the other side, 0.016 for toluene at 46.6°. Generally, the differences from one liquid to another are not larger than they are for the same liquid from one temperature to another. Likewise, in Table II., the average value of the constant is 1.022, with differences of 0.014 for ether at 20.0° on the one hand, and 0.011 for chlorbenzene on the other.

Introducing $c = 1.243$ from Table I. and $c = 1.022$ from Table II. into equation (A), and treating α as the unknown quantity, I calculated the capillary constants to be those given in Tables III. and IV., respectively, beside which are placed the corresponding data given by Ramsay and Shields[1] and Ramsay and Ashton.

TABLE III.

Comparison of Capillary Constants for Tubes A and B. $c = 1.234$.

Names of liquids.	Temp.	γ. $\gamma = chs. + s^2$.	γ. Ramsay & Shields.	$\gamma - \gamma$.
Water.....	30.0°	68.82	69.10	—0.28
"	40.0°	67.42	67.50	—0.08
Methyl alcohol.....	20.0°	23.39	23.03	+0.36
Ethyl alcohol	20.0°	22.17	22.03	+0.14

[1] *Loc. cit.*

Names of liquids.	Temp.	γ. $\gamma = chs. + s^2$.	γ. Ramsay & Shields.	$\gamma - \gamma$.
Acetone	16.8°	23.34	23.35	—0.01
"	46.4°	19.59	19.68	—0.09
Ethyl ether	20.0°	16.42	16.49	—0.07
" "	30.0°	15.18	15.27	—0.09
Ethyl iodide	19.1°	29.90	30.00	—0.10
Carbon bisulphide	9.7°	32.22	32.73	—0.49
Benzene	11.2°	29.31	29.21	+0.10
"	46.0°	24.75	24.21	+0.04
Chlorbenzene	9.5°	33.86	33.71	+0.15
"	45.6°	29.68	29.30	+0.38
Toluene	15.2°	27.96	28.18	—0.22
"	46.6°	24.25	24.60	—0.35

TABLE IV.

Comparison of Capillary Constants for Tubes B and C. $c = 1.022$.

Names of liquids.	T.	γ. $\gamma = chs + s^2$	γ'. Ramsay & Shields.	$\gamma - \gamma'$.
Acetone	16.8°	23.32	23.35	—0.03
"	46.4°	19.64	19.68	—0.04
Chlorbenzene	45.6°	29.56	29.30	+0.26
"	77.8°	26.01	25.66	+0.35
Ethyl ether	20.0°	16.42	16.49	—0.07
Benzene	11.2°	29.28	29.21	+0.07
"	46.0°	24.88	24.71	+0.11
Toluene	15.2°	27.93	28.18	—0.25
"	46.6°	24.46	24.60	—0.14
"	78.4°	21.09	20.93	+0.16

It is at once apparent that only in a few instances the differences between Ramsay and Shields' results and mine amount to more than a few tenths of a per cent., and in some cases the correspondence is as good as perfect. Furthermore, the differences that are found seem to be very nearly the same when either pair of tubes is employed; this indicates that the differences are due rather to the possible differing degrees of purity in the liquids employed by each of us than to a fault in the apparatus itself. However that may be, the data show that it is possible to obtain with the apparatus in question results, which by means of the formula (A), are comparable with those obtained by Ramsay and Shields or Aston. One cannot withstand the temptation to quote Jäger's words:[1] " ..... unsere

[1] *Loc. cit.*

methode is vollständig geeignet, richtige Resultate zuergeben. Fasst man noch die leichte, sichere und wenig zeit beanspruchende Handhabung, welche unser Apparat erfordert, ins Auge, so wird man wohl leicht zur Ueberzeugung gelangen, dass unter den gegenwärtigen Methoden für den praktischen Gebrauch kaum eine bessere zu finden sein dürfte." As to what pertains to the experimental handling of the apparatus, my experience with it enables me to subscribe to the above. But a restriction has to be made in regard to the conversion of the indirect results into direct ones. Jäger's formula has been shown above to be only approximately correct, and the one I propose has but an empirical basis. Although it has been found to stand the test of comparison with ten liquids of different properties, when two sets of tubes were employed, it is not allowable to claim that it will furnish reliable results for any liquid whatsoever. In other words, the instrument cannot be depended upon to give absolute data, since the "apparatus constant" may differ from liquid to liquid. Still it is not at all probable that the variations in the value of the "apparatus constant" will be very great in any case, and, as a variation of as much as ten per cent. has but a relatively small influence upon the surface tension, the method may be considered to give results accurate enough for the calculation of molecular masses, since Ramsay and Shields do not claim for their method an accuracy of more than six or seven per cent.

VI. MODE OF PROCEDURE IN DETERMINING THE MOLECULAR MASSES OF LIQUIDS.

In determining the molecular mass of a liquid it is well to measure its surface-tension at three different temperatures, and for this purpose vapor jackets will be found convenient.. Temperatures easy to get are (1) that of the atmosphere 10° to 25°; (2) that of boiling carbon bisulphide, about 46°; (3) that of boiling alcohol, about 78°. Of course, other liquids than these may be used, all that is required is that the temperatures obtained are 20°–30° apart.

The liquid is placed in the test tube *O*, and carbon bisulphide is poured into the jacketing tube. The capillary tubes are im-

mersed in the liquid, and, after the temperature has become uniform, several readings are made, their average being taken. The carbon bisulphide is now boiled and when the temperature has become constant a second series of readings is made. The flame is removed and, after the liquid has cooled down a little, alcohol is substituted for the carbon bisulphide. The alcohol is now boiled and a third series of readings taken when the temperature becomes stationary. All of these operations can be easily made in less than an hour.

It is possible to determine the specific gravity of the liquid at the different temperatures during the above operation, as the capillary apparatus requires but little continuous attention, most of the time taken up in a determination being needed in warming the liquid to a constant temperature. Any of the ordinary methods of density determinations may be employed which can give it to the third or fourth decimal place.

The necessary calculations may be illustrated by a couple of examples, one of a normal liquid, the other of an associated liquid. For the theoretical grounding and fuller explanation of the method, reference must be had to Ramsay and Shields' paper.[1]

BENZENE.

$$\gamma = chs + s^2 = (1.243 \times 25.86 \times 0.8871) + 0.80 = 29.31 \text{ dynes at } 11.2°.$$

$$= (1.243 \times 22.75 \times 0.85) + 0.72 = 24.75 \text{ dynes at } 46.0°.$$

$$\gamma(Mv)^{\frac{1}{3}} = (78/0.8871)^{\frac{1}{3}} \times 29.31 = 575.1 \text{ ergs at } 11.2°.$$

$$(78/0.8500)^{\frac{1}{3}} \times 24.75 = 501.8 \text{ " " } 46.0°.$$

$$\frac{d[\gamma(Mv)^{\frac{1}{3}}]}{dt} = \frac{575.1 - 501.8}{46.0 - 11.2} = \frac{73.3}{34.8} = 2.106.$$

The value assigned to the constant by Ramsay and Shields is 2.121, from which the constant just calculated differs by only 0.015; hence benzene is a normal liquid.

[1] *Loc. cit.*

ACETONE.

$\gamma = chs + s^2 = (1.022 \times 27.75 \times 0.7998) + 0.64 = 23.32$ dynes at 16.8°.

$(1.022 \times 24.22 \times 0.7656) + 0.59 = 19.55$ dynes at 46.4°.

$\gamma(Mv)^{\frac{1}{3}} = (58/0.7998)^{\frac{1}{3}} \times 23.32 = 406.1$ ergs at 16.8°.

$(58/0.7656)^{\frac{1}{3}} \times 19.55 = 351.6$ " " 46.4°.

$$\frac{d[\gamma(Mv)^{\frac{1}{3}}]}{dt} = \frac{406.1 - 351.6}{46.4 - 16.8} = \frac{44.5}{29.6} = 1.840.$$

The smallness of this constant indicates association in acetone. To determine the amount of association, we multiply the molecular mass M, by a factor x, which represents the average number of simple molecules that have coalesced to form a complex molecule. The calculation is as follows:

$$\left(\frac{2.121}{1.840}\right)^{\frac{1}{3}} = 1.25 \text{ between } 16.8° \text{ and } 46.4°.$$

the average molecular mass throughout this range of temperature is accordingly $1.25 \times 58 = 73$.

The apparatus described above was made by Walmsly, Fuller & Co., of Chicago, and has proven satisfactory in every detail. The makers inform me that they are ready to furnish the apparatus provided with a micrometer screw divided according to the metric as well as the English system.

ON THE REACTION BETWEEN CARBON TETRACHLORIDE AND THE OXIDES OF NIOBIUM AND TANTALUM.

BY M. DELAFONTAINE AND C. E. LINEBARGER.

Received April 20, 1896.

EUG. DEMARCAY[1] states that if the vapor of carbon tetrachloride be passed over the oxide of niobium or of tantalum heated below redness, the metallic oxides are converted into chlorides. "Dans le cas de l'acide niobique, la reaction se produit déja, bien qu' avec lenteur à la temperature de la naphthalene bouillante (280°) et avec une extréme rapidité à 440°."[2]

Now the chlorides of these rare elements enter into reaction

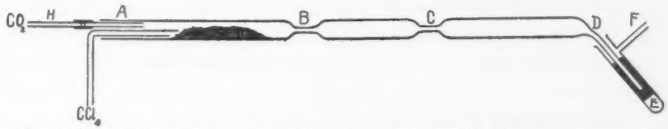
1 *Compt. Rend.*, 104, 111, *1887*.

2 *Loc. cit.*

very readily, and may serve as the starting points for numerous syntheses. Demarcay's statements led us to believe that the reaction in question would furnish a rapid method of obtaining these chlorides in quantity with comparative ease. On making use of the method, however, we found that the reaction does not take place in just the way indicated by Demarcay. We will first communicate our results obtained with niobic acid.

We used niobic pentoxide obtained from recrystallized potassium oxyfluosalt resulting from treatments of samarskite. The salt was decomposed in the usual way by sulphuric acid, boiled with water, and the residue ignited at strong red heat to expel the last traces of sulphuric acid.

The oxide was placed in one end of a piece of hard glass tubing, constricted in several places (Fig. 1), and the tube was heated in the vicinity of the oxide in a combustion furnace to



300°–400°. When the vapor of carbon tetrachloride was passed over the heated oxide, a reaction occurred immediately, and a yellowish white sublimate condensed in the cooler parts of the tube. If the oxide employed was quite pure, almost the totality of it could be converted into the volatile product. By careful application of heat it was possible to drive the sublimed substance into the further portions of the tube; it was then seen that the sublimate could be separated into two main portions, a more volatile one of a yellow color, and a less volatile one of a nearly white color. The properties of the yellow product were those of the pentachloride of niobium, while the properties of the whitish portion agreed with those of the oxychloride of niobium. By far the larger portion of the product of the reaction consisted of the oxychloride. The action of carbon tetrachloride on niobic acid seems to yield principally the oxychloride of niobium as the solid product; of the gaseous products formed, phosgene seemed to predominate.

It was thought that possibly the presence of even a slight

amount of air might exercise an oxidizing influence upon the pentachloride at the moment of its formation, converting it into the oxychloride. We accordingly carried out the same experiment in an atmosphere of carbon dioxide, but could not see that the proportion of the pentachloride was at all increased.

Again it was considered that the relative amount of the pentachloride might be made greater by allowing the reaction to take place in an atmosphere of chlorine, but even under such conditions the principal product was found to be the oxychloride.

We conceive then that the main reaction of carbon tetrachloride and niobic pentoxide may be represented by the equation

$$3CCl_4 + Nb_2O_5 = 2NbO.Cl_3 + 3COCl_2,$$

which illustrates again the tendency that niobium has to enter into combination as *niobyl*.

We have prepared a considerable quantity of niobyl chloride according to the above reaction, and, after numerous experiments, have adopted the following method of conducting the operation:

A tube of the shape indicated in the figure is prepared and filled with niobic pentoxide between *A* and *B*. As the chlorine compounds of niobium are quite voluminous, care has to be taken not to employ too much of the oxide; we found that for a tube of about two cm. bore and having a length of about forty cm. between *A* and *B*, ten to fifteen grams could be taken. The tube is placed in a combustion furnace and the portion in the vicinity of the oxide heated to about 400°. A current of dry carbon dioxide is now passed through the tube to dry it thoroughly and expel the air. The constrictions at *B* and *C* are heated nearly to redness to prevent their becoming stopped up, and carbon tetrachloride is gently distilled over upon the niobium compound. It is advisible to discontinue the current of carbonic acid by pinching the delivery tube together at *H*, since often the pressure of the tube becomes sufficient to throw the acid out of the generator. In the early stages of the operation, there occurs a transportation of substance in such a fine state of division that it is carried clear through the tube; in

order to prevent its entering the wash bottle containing sulphuric acid, and connected at *F*, a little glass wool or asbestos fiber is packed around the end of the tube in *E*. When *BC* becomes nearly filled with the products of the reaction, it is heated to a temperature just sufficient to volatilize the pentachloride, which may then be driven over into *CD*, leaving almost pure oxychloride in *BC*. When the reaction is at an end, no more carbon tetrachloride is passed into the tube, but the current of carbon dioxide is again sent through it in order to aid in the separation of the pentachloride from the oxychloride of niobium. Any carbon tetrachloride that may have condensed in *CD* is driven over into *E*, and *BC* and *CD* are so heated that the pentachloride passes through the constriction *C* and condenses just in front of *D*. While it is possible to drive almost all of the pentachloride out of *BC* and thus to obtain almost pure oxychloride, there is always a not inconsiderable portion of the latter compound that finds its way into *CD*.

In several experiments we found that a small quantity of an orange-colored sublimate collected at the further end of *CD*, which circumstance proves that this substance is more volatile than the pentachloride of niobium. H. Rose[1] also observed the formation of such a colored product when he was engaged in the investigation of chlorine on an intimate mixture of charcoal and tantalic acid. He found that if the acid employed contained "nur die geringste Spur von Wolframsäure, so zeigt sich bei der Darstellung des Chlorids eine sehr kleine Menge von einem rothem Chloride, das etwas flüchtiger als das Tantalchlorid ist." The compound is probably the oxytetrachloride of tungsten, its formation being due to a slight contamination of our niobic acid with a tungsten compound.

When we passed the vapor of tetrachloride over tantalic acid, no reaction took place at a lower temperature than 400°, when a small amount of volatile substance was formed, which soon ceased, however. Even on heating to a temperature high enough to cause the Bohemian glass tube to soften, we did not obtain any more of the sublimable product. The tantalic oxid turned yellow and assumed a pasty condition. It is probable that the

[1] *Ann. chem. phys., Pogg.*, 99, 75, 1856.

sublimed substance consisted of the chlorine compounds of niobium, since it is quite possible that our tantalic oxid was not entirely free from an admixture of niobic oxid. This behavior suggests a method of purification of tantalic acid containing a little niobic acid; we will not lay much stress on this, however, untll we have done more work on the subject.

The readiness with which niobium oxychloride was formed in all our experiments contrasting with the comparatively small quantity of the pentachloride obtained illustrates once again the great inclination niobium has to enter into combination not as an individual element, but in the form of the radical *niobyl*. The actio.n of sulphur and chlorine on NbO, investigated by Delafontaine, the numerous series of oxyfluo-salts prepared by Marignac, and the decomposition of niobyl chloride by magnesium are other facts of the same import. In this respect the analogy of niobium aud vanadium is very striking, but it is almost entirely lacking in niobium and tantalum.

THE CHEMICAL NATURE OF DIASTASE.[1]

SECOND PAPER.

By Thomas B. Osborne and George F. Campbell.

Received May 15, 1896.

In a former paper, by one of us,[2] the results of some attempts to isolate diastase have been detailed. This work has been continued, but as yet no preparations of diastase have been realized more active than those there described. The results given in the former paper, however, have been confirmed, and details of the process for obtaining highly active diastase have been determined more exactly.

Here follows a concise account of this later work so far as it is worth placing on record.

Fifteen kilograms of fine ground malt were treated with thirty liters of five per cent. sodium chloride brine, and after standing some time, with frequent stirring, the extract was pressed out and filtered, yielding sixteen liters of clear filtrate. The meal residue was again treated with fifteen liters of five per cent. brine

[1] From the Report of the Connecticut Agricultural Experiment Station for 1895.

[2] Eighteenth Annual Report of this Station, pp. 192-207; *J. Am. Chem. Soc.*, 17, 587-603.

and fifteen liters more of clear extract obtained. The united solutions were then saturated with ammonium sulphate and the precipitate filtered out, dissolved in brine and filtered perfectly clear. This liquid was saturated with ammonium sulphate, the precipitate was suspended in two liters of water and dialyzed two days. The ammonium sulphate which adhered to the precipitate, at first prevented solution of the substance, but after two days enough sulphate was removed by dialysis to allow the proteid to dissolve. The solution was filtered clear and dialyzed seven days longer. The globulin thus precipitated was filtered out and the solution, which measured 5800 cc., was dialyzed into an equal volume of alcohol of 0.86 sp. gr. for eighteen hours. The precipitate, VI,[1] was filtered out and the solution, which then measured 3500 cc., was again dialyzed into an equal volume of alcohol of 0.86 sp. gr. for eighteen hours yielding precipitate VII. The filtrate from VII measured 2700 cc. and was dialyzed into an equal volume of alcohol of 0.86 sp. gr. for eighteen hours, giving precipitate VIII, the filtrate from which measured 2000 cc. and was dialyzed into 2500 cc. of alcohol of 0.82 sp. gr. for eighteen hours. This gave precipitate IX, the filtrate from which measuring 1800 cc. was dialyzed into twice its volume of alcohol of 0.81 sp. gr., giving precipitate X. The solution filtered from X was then treated with absolute alcohol until nothing further separated, giving precipitate XI.

These six fractions were all, separately, treated with water; X and XI dissolved completely, the others partially. The aqueous solutions, filtered clear, containing the proteoses and albumin of the six fractions, were then separately dialyzed into water, to remove all freely diffusible substances and, as no globulin was precipitated from any of them, the dialyzers were transferred to alcohol, in order to concentrate their contents, and absolute alcohol was finaly added until the proteids were completely thrown down.

In this way six preparations were obtained, which, when dehydrated with absolute alcohol and dried over sulphuric acid, weighed respectively, 18, 1.37 gram; 19, 1.47 gram; 20, 4.05

[1] The precipitates and preparations described in this paper are numbered consecutively with those specified in the former article on Diastase: This Journal, 17, 587.

grams; 21, 4.82 grams; 22, 2.17 grams; and 23, 0.63 gram.

The disastatic power of these preparations was determined in the manner described in the former paper,[1] and found to be as follows: 18 — 0; 19 = 60; 20 = 300; 21 = 300; 22, trace, and 23 = 0.

It will be noticed that nearly all the enzyme was thrown down in fractions 8 and 9, which gave preparations 20 and 21. These were but half as active as preparation 15, described in the former paper.

In order to purify this diastase, 20 and 21 were united, dissolved in 100 cc. of water, the insoluble matter filtered out and washed with thirty-five cc. of water (these first washings being added to the filtrate), then with more water, and finally with absolute alcohol. Dried over sulphuric acid, this preparation, 24, weighed 0.23 gram. The filtrate and first washings from 24 were treated with 200 cc. of alcohol of 0.885 sp. gr., making a solution containing 36.5 per cent. of alcohol. A small precipitate resulted, 25, which when filtered out and dried over sulphuric acid, weighed 0.25 gram, and had a diastatic value of 15. The filtrate from this precipitate was mixed with 160 cc. of alcohol of 0.84 sp. gr., raising the per cent. of alcohol to 50.7, and the precipitate, 26, thus produced when dried as usual weighed 2.35 gram and had a diastatic value of 86. To the filtrate from 26, 100 cc. of alcohol of 0.84 sp. gr. and 100 cc. of absolute alcohol were added, raising the alcohol-content to 61.6 per cent. The precipitate, 27, which resulted, was filtered out, weighed 2.87 grams and had a diastatic value of 600, just twice that of 20 and 21, from which it had been derived, and just equal to that of the most active preparation, 15, of the former paper. To the filtrate 200 cc. of absolute alcohol were added, giving a precipitate, 28, which weighed 1.00 gram and had a diastatic value of 100.

The filtrate from 28 mixed with 200 cc. more of absolute alcohol, gave a precipitate, 29, which weighed 0.40 gram and showed only a trace of disastatic power. The filtrate from 29, mixed with 400 cc. of absolute alcohol, yielded 0.17 gram of substance, 30, that was totally inactive, and the filtrate from

[1] Report of Conn. Expt. Station for 1894, p. 194; *J. Am. Chem. Soc.*, 17, 587.

this when evaporated to dryness left a residue weighing 0.65 gram.

The results of this experiment showed that little diastase was precipitated by bringing the alcohol-content of the malt extract to fifty per cent. by weight, while nearly all the diastase was thrown down, under the conditions described, when the proportion of alcohol in the malt extract was made sixty per cent.

In order to still further concentrate or purify the diastase contained in precipitate 27, this was treated with 100 cc. of water and, without filtering from the substance which had been coagulated by precipitation and drying, 100 grams of absolute alcohol were added. The precipitate so produced was filtered out and extracted with water. The insoluble matter, after washing and drying, weighed 0.50 gram. The aqueous filtrate, from this insoluble matter, was then completely precipitated with absolute alcohol and 0.45 gram of substance, 31, obtained having a diastatic value of 200. The solution, filtered from the first precipitate, produced by adding an equal weight of alcohol to the solution of 27, as just described, was mixed with enough absolute alcohol to raise this ingredient to fifty per cent., and the substance thereby thrown down, 32, weighed, when dry, one gram, and had a diastatic value of 400. The filtrate from 32 was completely precipitated with absolute alcohol and yielded two-tenths gram of inactive proteid. It is thus seen that the diastase instead of increasing in power under this treatment declined to two-thirds of its original in activity.

Having thus learned more exactly the conditions under which diastase may be so far separated from the other malt proteids, an attempt was made to prepare a large quantity of material with which to carry the purification farther. Through the kindness of Mr. C. Von Eggloffstein, of the Maltine Manufacturing Company, at Yonkers, N. Y., a considerable supply of malt extract, rich in diastase, was placed at our disposal. For this favor and much information respecting malt extracts, we wish to express our especial thanks.

One gallon (3,785 cc.) of this malt extract, which had been concentrated at a low temperature *in vacuo* until it contained about fifty per cent. of solid matter, was dialyzed into water for

forty-eight hours, whereby a large part of the sugar was removed and a thin liquid remained. This was saturated with ammonium sulphate and the precipitated proteids were filtered out, suspended in water and dialyzed for five days. To the liquid contents of the dialyzer, filtered clear from insoluble matters, alcohol was added to make fifty per cent. of the resulting mixture. This threw down a precipitate which was filtered out, dehydrated with absolute alcohol, and dried over sulphuric acid.

This white, easily-powdered precipitate, XII, weighed ninety-five grams. One-half of it was insoluble in water and salt solution. By extraction with water and precipitation with alcohol, added first to fifty per cent. and afterward to sixty per cent., two preparations, 33 and 34, resulted, weighing respectively 4.85 grams and 7.21 grams, that had little diastatic power.

The solution from which the first precipitate, XII, had been separated was treated with enough alcohol to make seventy-five per cent., and the resulting precipitate, XIII, filtered out and found to weigh, when dried over sulphuric acid, seventy grams. This precipitate included the chief part of the diastase of this extract. It dried to a light, dusty powder of pale straw-yellow color, almost entirely soluble in water and had a diastatic value of 200.

XIII was dissolved in water and fractionally precipitated, but, for some unknown reason, the resulting fractions were almost entirely inactive.

In another attempt to make a large quantity of diastase, three gallons (11.4 liters) of the highly concentrated malt extract were mixed with half their weight of water and enough alcohol to make a mixture containing forty-six per cent. of alcohol. A very large precipitate, XIV, resulted, which was filtered out, and as it consisted almost entirely of insoluble matter (probably globulin), it was not further examined.

The filtrate from precipitate XIV was treated with alcohol, raising the strength to sixty per cent; the precipitate so produced was filtered out and, as it contained a large amount of sugar, it was dissolved in about five liters of water, the resulting solution was saturated with ammonium sulphate, the precipitate filtered out, suspended in one liter of water and dialyzed

for five days. The precipitate in the dialyzer was filtered out and the clear solution was treated with alcohol sufficient to make fifty per cent. of the resulting mixture, but as only a little substance separated, the amount of alcohol was increased to sixty per cent. This threw down a considerable precipitate, XV, which, when dehydrated with absolute alcohol and dried over sulphuric acid, weighed fifty-seven grams and had a diastatic value of 300.

Numerous attempts were made to obtain from portions of precipitate XV, by fractional precipitation with alcohol, diastase of greater power than 300, but without success.

Several hundred trials were made with the object to determine precisely the influence of certain conditions, such as the age of the diastase solution, and of certain substances, added in systematically varied quantities, especially sodium chloride, disodium orthophosphate, tripotassium orthophosphate, orthophosphoric acid, acetic acid, and citric acid (using the amount of copper reduction as the measure of effect), but, while the results were decisive in some cases, *e. g.*, citric acid, in the minutest quantities, always depressed or destroyed diastatic action, in the majority of instances, no such uniform results were attainable as would lead to safe conclusions in regard to the circumstances that insure a high degree of diastatic activity.

From our experience in testing these preparations it would seem that the purer the diastase is made, the more sensitive it is to external conditions, and that the method of testing the purity of the ferment by its maltose-producing power thus becomes of uncertain value and perhaps fails to furnish a safe criterion of the purity of the enzyme. That the proteid is not the only factor involved in the amylolytic action of diastase is indicated by the great influence on its activity that often accompanies the addition of various substances to its solution. In view of these facts it is not at all improbable that in thus attempting to purify diastase we remove some substance that favors, or is essential to its action, and that we may have in hand what may be properly termed the enzyme itself, which is feeble in its operation through the absence of deficiency of some accessory substance. Thus the addition of sodium chloride in

many cases increases the diastatic action several fold. That the albumin is an essential factor in diastatic action could not be positively proved, but the results of further experience have tended to strengthen this belief. Of all the preparations that we have made, none from which albumin was absent showed amylolytic power, and those containing the most albumin were the most active. It was always possible to roughly judge of the diastatic power of a preparation, by heating a portion of its solution to 65° C. and observing the amount of coagulum formed.

The fact that active diastase was obtained only from solutions whose alcohol content lies between fifty and sixty per cent., may, we think, be regarded as probable evidence that the enzyme is not something carried down mechanically with the proteid.

THE PROTEIDS OF MALT.[1]

By Thomas B. Osborne and George F. Campbell.

Received May 15, 1896.

As is well known, water extracts a considerable quantity of proteid matter from ground malt. This we find to consist of at least five distinct bodies, namely, a globulin, an albumin and three proteoses. Whether true peptones are present was not determined, for the malt extracts are so strongly colored that the biuret test entirely fails. Besides the proteids soluble in water another exists that may be taken up by dilute alcohol (of 0.9 sp. gr.). After extracting malt with saline solutions and alcohol, a further quantity of proteid matter remains, the nature of which we have not been able to determine.

Malt-Globulin.—Ten kilograms of air-dried malt, freshly prepared by ourselves in the laboratory, and ground to a fine meal were treated with twenty liters of water and, after standing three hours, were squeezed out in a press and the solution filtered clear. The residual meal was treated with eight liters more of water and the second solution was pressed out and filtered. The united solutions were saturated with ammonium sulphate, the precipitate was suspended in about four liters of water and dialyzed for three days, when it dissolved, with the exception of a

[1] From the Report of the Connecticut Agricultural Experiment Station for 1895. Communicated by the authors.

slight residue. In order to reduce its volume and separate impurities, the filtered solution was again saturated with ammonium sulphate, the precipitated substance was suspended in 1500 cubic centimeters of water and dialyzed until the greater part of the ammonium sulphate had been removed, when the solution was filtered clear. The matters now remaining undissolved were treated with ten per cent. salt solution to extract any soluble globulin which might have been deposited during dialysis, and the substance not taken up in salt-solution was filtered out. This last unquestionably consisted almost entirely of insoluble globulin, but as it separated from an unfiltered solution and was small in quantity it was not further examined. The salt-solution was then dialyzed free from chlorides, and the globulin thus precipitated was filtered out, washed with alcohol and dried over sulphuric acid. But 0.5 gram of substance was obtained which, dried at 110°, gave 0.93 per cent. of ash and, reckoned ash-free, 15.70 per cent. of nitrogen. This was marked preparation 1.

The solution of the ammonium sulphate precipitate, containing the bulk of the malt-proteid, from which the insoluble matter yielding preparation 1 had been filtered, was dialyzed, first, into water, until the salts were mostly removed, and then into an equal volume of alcohol of 0.84 sp. gr. for forty-eight hours. The proteid thus precipitated was filtered out and the filtrate was dialyzed into alcohol. After filtering out the second precipitate, the filtrate was dialyzed into stronger alcohol, and this process was repeated, thus depositing the proteids in four fractions, a fifth being obtained by adding absolute alcohol to the remaining solution as long as anything was thrown down. Each of these five fractions was then treated with water to dissolve albumins and proteoses and the resulting solutions were dialyzed in water for several days. The first four fractions were but partly soluble in water, and accordingly, the insoluble parts, after washing with water, were treated with ten per cent. sodium chloride solution, and the portion which in each case remained undissolved was filtered out, washed thoroughly with water and alcohol and dried at 110° for analysis. The four saline extracts were then dialyzed, bnt those from the third and fourth fractions were

found to contain only trifling quantities of proteids. That from the second fraction gave no precipitate of globulin on dialysis, but by adding alcohol to the solution 0.49 gram of preparation 2 was obtained, having 4.33 per cent. of ash and, calculated ash-free, 15.18 per cent. of nitrogen. The sodium chloride extract from the first fraction gave a precipitate on dialysis which, after washing with water and with alcohol, weighed one and two-tenths grams, 3.

The filtrate from 3, by precipitation with alcohol, yielded 4, weighing 1.54 grams.

After extracting the four fractional precipitates with water and with salt solution, the undissolved residue, in each case, was washed thoroughly with salt solution, with water and with alcohol and dried over sulphuric acid, giving, in the order named, preparation 5 weighing eight grams, 6 weighing five grams, 7 weighing 2.87 grams, and 8 weighing nine-tenths gram. These preparations, dried at 110°, had the following composition:

MALT-GLOBULIN, BYNEDESTIN.

	3.	4.		5.	6.	7.	8.
Carbon....	53.11	53.58		53.55	53.51	53.25	53.42
Hydrogen.	6.45	6.70		7.01	6.75	....	7.15
Nitrogen..	15.78	15.86	15.87	15.72	15.87	16.12	16.65
Sulphur }	24.66	23.86		1.23	1.12	1.38	} 22.78
Oxygen }				22.49	22.75		
	100.00	100.00		100.00			100.00
Ash.....	0.75	1.43		1.09	0.66	0.55	0.24

Preparations 5 and 6 have the same composition as the globulin 3 and 4 obtained from the sodium chloride extracts of the fractional precipitates, while 8 contains nearly one per cent. more nitrogen, and as will be seen later, has nearly the same composition as malt albumin and is unquestionably for the most part albumin coagulated by the action of the alcohol. 7 appears to be a mixture of coagulated globulin and albumin. In a similar manner three other preparations of the coagulated globulin 9, 10 and 11 were obtained from another lot of malt.

MALT-GLOBULIN, BYNEDESTIN.

	9	10	11
Carbon	52.90	52.99	53.15
Hydrogen	6.74	6.64	6.52
Nitrogen	15.33	15.31	15.81
Sulphur	1.17	25.06	1.47
Oxygen	23.86		23.05
	100.00	100.00	100.00
Ash	0.44	0.32	0.23

Preparations 9 and 10 are lower in carbon and nitrogen than those just described, probably because, having been prepared in a smaller quantity, they carried down a larger proportion of impurities when thrown out of solution by alcohol.

From a malt extract that had been concentrated *in vacuo* at a low temperature, for which we are indebted to Mr. C. von Egloffstein, alcohol, added to make forty-six per cent. by weight of the mixture, threw down a large quantity of coagulated globulin that was not further examined, the filtrate from which, on increasing the content of alcohol to sixty per cent., gave a second precipitate that was largely soluble in water. It was accordingly mixed with water and with ammonium sulphate in excess, and the substance thus thrown down was suspended in a liter of water and dialyzed for five days. The insoluble residue in the dialyzer, when washed with water and alcohol, gave preparation 12, weighing 26.78 grams. From this same extract by fractional precipitation with alcohol another small preparation of coagulated globulin, 13, was obtained.

SUMMARY OF ANALYSES OF MALT-GLOBULIN, BYNEDESTIN.

	1	2	3	4	5	6
Carbon			53.11	53.58	53.55	53.51
Hydrogen			6.45	6.70	7.01	6.75
Nitrogen	15.70	15.18	15.78	15.86	15.72	15.87
Sulphur					1.23	1.12
Oxygen			24.66	23.86	22.49	22.75
			100.00	100.00	100.00	100.00

	9	10	11	12	13
Carbon	52.90	52.99	53.15	53.04	52.96
Hydrogen ...	6.74	6.64	6.52	6.57	6.83
Nitrogen	15.33	15.31	15.81	15.94	15.96
Sulphur ...	1.17		1.47		
Oxygen ...	23.86	25.06	23.05	23.61	24.25
	100.00	100.00	100.00	100.00	100.00

Although considerable differences exist among these analyses, they agree with each other as well perhaps as could be expected considering the difficulty of preparing the substance in a state of purity.

Whether other globulins occurred in the malt could not be determined by fractional precipitation owing to the small total quantity of globulin present.

The malt residue remaining after extracting with water, in the case first described, was treated with ten per cent. salt solution and the clear filtered liquid was dialyzed until free from chlorides. The precipitated globulin was filtered out, washed with water and alcohol and dried over sulphuric acid. This preparation, 14, weighed 4.12 grams and had the following composition :

MALT-GLOBULIN, BYNEDESTIN.

	14		
	I.	II.	Average.
Carbon	52.94	52.78	52.86
Hydrogen	6.87	6.79	6.83
Nitrogen.....	16.16	16.18	16.17
Sulphur	1.14		1.14
Oxygen.....			23.00
			100.00
Ash.....	0.96		

It is to be noted that the carbon is a little lower and the nitrogen higher than the average of the figures previously obtained. This is perhaps due to presence of a little edestin,[1] the globulin of ungerminated barley. Edestin is not readily soluble in dilute saline solutions, such as are formed on treating seeds with water, and, if occurring in the malt, ought to be present in the salt extract of the meal after it has been exhausted with water.

[1] Annual Report of Conn. Agr. Expt. Station for 1894, p. 172, and Journal of American Chemical Society, 17, 545.

Owing to the incomplete extraction with water, the preparation obtained in this case should be a mixture of the two globulins, if both are present. Edestin can only occur in extremely small quantity in malt, since but 4.12 grams of globulin were obtained by extracting ten kilograms of malt with salt solution after treatment with water, and most of this consisted of the more soluble globulin first described. It is interesting to note the practically complete disappearance of edestin during germination and the formation of the more soluble globulin with three per cent. less nitrogen and two per cent. more carbon. It is, of course, not demonstrated that the malt globulin is derived from edestin, but that the proteids undergo extensive changes before conversion into proteoses and peptones is very evident.

When dissolved in considerable quantity in salt solution, bynedestin is precipitated by water, is not precipitated by saturation with sodium chloride, and but partly by saturation with magnesium sulphate. With the biuret test it gives a violet color. Dissolved in ten per cent. sodium chloride solution and heated to 65°, a turbidity is produced which increases to flocks at 84°. The coagulum gradually augments as the temperature rises but, after heating to 100°, the filtrate from the coagulum yields an abundant precipitate on adding dilute hydrochloric acid. The solution in ten per cent. sodium chloride brine gives a precipitate with acetic acid which is soluble in an excess of the acid. These reactions show that this body is in no sense a proteose, but has characters common to plant globulins. Bynedestin formed about sixty per cent. of the total water-soluble proteid matter in the malt extract first described in this paper. Out of a total of 33.27 gram of proteid recovered in the different preparations from 10,000 grams of malt, 19.88 grams consisted of bynedestin.

Malt Albumin, Leucosin.—Under the name leucosin, one of us has described an albumin occurring in small quantity in the seeds of wheat, rye and barley. In the aqueous malt-extracts an albumin is found identical with leucosin in properties and composition. As stated in previous papers, this albumin is so intimately associated with diastatic action as to make probable that it is either diastase itself or an essential factor in diastatic

amylolysis. In attempts to fractionally separate malt-leucosin from the associated proteids, many preparations have been made which are mixtures of leucosin with proteose. In several cases these mixtures have been analyzed and have so nearly the composition of leucosin as to make certain that one of the proteoses of malt has very nearly the same ultimate composition as the albumin. Analyses of these mixtures may therefore be taken to represent the composition of either of these proteids.

In the extraction first described in this paper, two preparations, 15 and 16, of albumin coagulated by alcohol, were obtained from solutions out of which the globulin had been precipitated by alcohol. If, as is invariably assumed, proteose cannot be rendered insoluble by contact with alcohol, these preparations may be taken to represent the composition of malt albumin. Their composition is here compared with that of leucosin coagulated by heat.

	Leucosin.		
	Malt.		Wheat, rye and barley. Average.
	15	16	
Carbon	53.23	52.90	52.93
Hydrogen	6.64	6.79	6.80
Nitrogen	17.00	16.41	16.70
Sulphur	23.13	23.90	1.37
Oxygen			22.20
	100.00	100.00	100.00
Ash	0.84	0.55	

The following figures give the composition of preparations derived from three different samples of malt. These were all obtained by precipitating the proteids with ammonium sulphate, dissolving the precipitates in water, dialyzing away the greater part of the salt and fractionally precipitating the solutions with alcohol. The fractions were dissolved in water as far as possible, filtered from the undissolved globulin and the aqueous solutions dialyzed for several days in water and then in alcohol. The proteids thus precipitated were mixtures of proteose and albumin. It will be noted that they all agree fairly well with one another and with leucosin in composition. Since these mixtures contained

from six and a half to fifty per cent. of albumin, it is evident that the two proteids have a very similar composition.

MALT LEUCOSIN AND PROTEOSE.

	17	18	19	20	21	22	23	24
Carbon	53.16	53.19	52.80	52.50	52.38	52.85	52.61	52.55
Hydrogen	7.03	6.71	6.96	6.72	6.63	6.67		
Nitrogen	16.50	16.60	16.09	16.10	16.51	16.25	16.35	16.41
Sulphur }	23.31	1.38	1.45	24.68	24.48	24.23		
Oxygen }		22.12	22.70					
	100.00	100.00	100.00	100.00	100.00	100.00		
Ash	0.84	0.78	0.59	0.66	1.55	0.22	0.51	

The preparations containing the most albumin, when dissolved in water, became turbid on heating to 50° and formed flocculent coagula at 58°. By saturating their solutions with magnesium sulphate the albumin was completely thrown out, and together with it much of the proteose. Saturating solutions of these preparations with sodium chloride, gave no precipitate when they contained but little albumin, but a heavy precipitate appeared on adding acetic acid to the salt-saturated solution. Solutions of the preparations containing much albumin gave precipitates on saturating with sodium chloride.

PROTEOSES OF MALT.

The proteose associated with albumin has the properties of a *protoproteose*, since it is readily and abundantly precipitated from its salt-saturated solution on adding acetic acid.

When malt extract is fractionally precipitated with alcohol a considerable quantity of proteose is thrown down before the albumin, so that the water-soluble part of the first fraction is chiefly proteose. The proportion of albumin in the precipitates increases as the alcohol is made stronger up to the point where it is all precipitated. At this stage much proteose remains dissolved which behaves differently from that first thrown down. A large quantity of concentrated malt extract was precipitated by alcohol added to 60 per cent., and after filtering, the proportion of alcohol was raised to seventy-two per cent. The substance thereby precipitated, when dried over sulphuric acid, weighed thirty-eight grams. This was dissolved in water, the solution was heated to boiling,

the coagulated albumin was filtered out and twenty per cent. of sodium chloride added to the solution. This caused a slight precipitate which was evidently the alcohol-soluble proteid, to be described later. The filtrate from this substance was then treated with a little acetic acid, which produced a copious precipitate that was filtered out and dissolved in water. This solution, exactly neutralized with sodium carbonate and fully saturated with salt, yielded a considerable precipitate, which was filtered out, dissolved in water and dialyzed free from chlorides.

A very small deposit, consisting of minute spheroids, was found in the dialyzer. This dissolved readily in exceedingly dilute salt solution, from which it was thrown down by much water. On adding nitric acid to the solution of this substance a precipiate was produced that dissolved on warming and reappeared on cooling, gave a clear pink biuret reaction and was precipitated by copper sulphate. On boiling its solution not even a turbidity was produced. Except for its behavior on heating, this substance has all the reactions of a *heteroproteose*. The amount obtained was exceedingly small, only enough for the above reactions. The solution filtered from this heteroproteose was concentrated by gently boiling over a low flame.

During concentration of the solution filtered from the heteroproteose a coagulum developed as a film on the surface of the liquid and sides of the dish. We have frequently noticed that plant proteoses from various seeds coagulate in this manner although behaving in most other respects like typical proteose. This coagulum, 25, filtered out washed with water and alcohol and dried over sulphuric acid, weighed 0.29 gram and contained 16.84 per cent. of nitrogen.

The filtrate from 25 was precipitated by alcohol and gave 1.45 gram of 26, having the following composition, when dried at 110°:

MALT PROTEOSE, 26.

	I.	II.	Average.
Carbon	50.61	50.64	50.63
Hydrogen	6.72	6.61	6.67
Nitrogen	16.69	....	16.69
Sulphur, Oxygen	....	....	26.01
			100.00
Ash	....	....	1.29

As will be remembered, in making these preparations, 25 and 26, the proteose was precipitated, first, by adding acetic acid to the solution containing twenty per cent. of salt and, second, by dissolving the precipitate thus produced in water and saturating the neutralized solution with salt. The filtrate, A, from the first, as well as the filtrate, B, from the second precipitation, still contained proteose.

A was therefore neutralized with sodium carbonate and saturated with salt, but, as no precipitate resulted, acetic acid was added as long as any proteid was thrown down.

B was treated similarly with acetic acid and the two precipitates thus obtained from the salt-saturated solutions were collected on the same paper and the filtrates were united and marked C. The precipitates were dissolved in water, the solution carefully neutralized, dialyzed free from chlorides and then concentrated by slow boiling. During concentration a small coagulum separated which was filtered out, washed with water and alcohol and dried over sulphuric acid. This preparation, 27, weighed 0.22 gram and contained, without correcting for ash, 16.40 per cent. of nitrogen.

An excess of alcohol was added to the filtrate from 27, and the precipitate produced, after treating in the usual manner, gave 1.49 gram of preparation 28, which, dried at 110°, had the following composition:

MALT PROTEOSE, 28.

	I.	II.	Average.
Carbon	49.82	49.87	49.85
Hydrogen	6.69	6.64	6.67
Nitrogen	16.00	....	16.00
Sulphur, Oxygen	....	....	27.48
			100.00
Ash	....	....	1.54

The salt-saturated filtrate, C from which 27 and 28 had been precipitated, was neutralized and dialyzed until much of the salt had been removed, then concentrated and dialyzed until free from chloride. The solution was finally concentrated to small volume and precipitated with alcohol. The substance so

obtained, after treating as usual, weighed 6.25 grams but was found to contain 4.70 per cent. of ash and only 8.91 per cent. of nitrogen, reckoned ash-free. This precipitate, which was expected to contain *deuteroproteose*, evidently included much non-proteid matter.

It will be noticed that of the thirty-eight grams of substance taken, only a very small part was recovered. It is probable that a large share of the substance (p. 550) was non-proteid, and also that during the dialysis much proteose was lost by diffusion.

Preparation 26 has the properties of a protoproteose and may be regarded as such. Preparation 28 is a mixture of proto- and deuteroproteose. Pure deuteroproteose was not obtained, it having been impossible to separate the non-proteid substances associated with it.

It thus appears that at least two protoproteoses exist in malt, for 26 has much less carbon than the mixtures of proteose and albumin, 17 to 24. Preparation 17 contains about ninety-five per cent. of proteose and has 53.16 per cent. of carbon, whereas 26 has only 50.63 per cent. of carbon. This difference can scarcely be due to non-proteid impurities, for 26 contains even more nitrogen than 17. According to the definitions now accepted, a protoproteose is any form of proteid which is soluble in pure water, uncoagulable by heat, precipitable by saturation with sodium chloride, and gives a pink biuret reaction and a precipitate with nitric acid that dissolves on warming and reappears on cooling. The protoproteoses obtained by artificial digestion, usually have a composition varying with that of the proteids from which they are derived, and the proteoses of malt may also be expected to differ according as they originate from one or another of the several proteids of barley. While the plant proteoses resemble the digestive proteoses in the reactions just specified, some of their physical properties are so different that it is not improbable that they are quite distinct substances.

MALT PROTEID SOLUBLE IN DILUTE ALCOHOL. BYNIN.

Three kilograms of ground malt were extracted with alcohol of 0.90 sp. gr. The extract was filtered clear, and concentrated to about one-third its original volume, on a water bath.

When cool the solution was poured off from the separated proteid and the latter was washed with dilute salt solution, with water, with ether to remove adhering water, and finally with absolute alcohol. Dried over sulphuric acid, this preparation, 29, weighed 33.1 grams, being 1.11 per cent. of the malt.

Dried at 110° it had the following composition:

	Bynin, 29.		
	I.	II.	Average.
Carbon	55.01	54.93	54.97
Hydrogen	6.77	6.49	6.63
Nitrogen	15.98	16.13	16.06
Sulphur	0.94	....	0.94
Oxygen	....	....	21.40
			100.00
Ash	....	....	0.67

In order to fraction this substance, twenty-seven grams were dissolved in alcohol of 0.70 sp. gr., the solution filtered perfectly clear, concentrated to small volume and poured into absolute alcohol, a few drops of ten per cent. salt solution being added to cause the proteid to separate. The precipitate so produced was filtered out, treated with absolute alcohol and dried over sulphuric acid. This preparation, 30, weighed twenty grams, and when dried at 110° had the following composition:

	Bynin, 30.		
	I.	II.	Average.
Carbon	54.74	55.08	54.91
Hydrogen	6.61	6.62	6.62
Nitrogen	16.21	16.06	16.14
Sulphur	0.83	....	0.83
Oxygen	....	....	55.07
			100.00
Ash	....	....	0.40

Of preparation 30, sixteen grams were dissolved in 180 cc. of warm alcohol of fifty per cent. by volume, and a part of the proteid precipitated by cooling to 0° C. The solution was decanted and the precipitate, 30*a*, was treated as just described for 30. The substance now separated, 30*b*, was treated in the same manner. 30*c*, thus obtained, was dissolved in a little strong

alcohol and the perfectly clear solution poured into absolute alcohol, adding also a few drops of ten per cent. salt solution. The precipitate was then dehydrated with absolute alcohol and dried over sulphuric acid. This preparation, 31, weighed eight and three-tenths grams and gave the following results on analysis :

BYNIN, 31.

	I.	II.	Average.
Carbon	55.07	....	55.07
Hydrogen	6.75	....	6.75
Nitrogen	16.18	16.42	16.30
Sulphur	0.84	....	0.84
Oxygen	....	....	21.04
			100.00
Ash	....	....	0.10

The solutions containing fifty per cent. of alcohol, which had been decanted from 30*a*, 30*b* and 30*c* were united, concentrated to small volume, cooled, and the liquid poured off from deposited substance. The latter, dehydrated with absolute alcohol and dried over sulphuric acid—preparation 32—weighed five grams.

As seen from the following table, these analyses show that the proteid has not been separated into fractions of differing composition.

SUMMARY OF ANALYSIS OF BYNIN.

	29.	30.	31.	32.	Average.
Carbon	54.67	54.91	55.07	55.16	55.03
Hydrogen	6.63	6.62	6.75	6.67	6.67
Nitrogen	16.06	16.14	16.30	16.53	16.26
Sulphur	0.94	0.83	0.84	0.76	0.84
Oxygen	21.40	21.50	21.04	20.88	21.20
	100.00	100.00	100.00	100.00	100.00
Ash	0.67	0.40	0.10	0.16	

These figures are, except for hydrogen, in remarkably close agreement with those given by Chittenden and Osborne for the composition of zein, the alcohol soluble proteid of maize ; but in properties the two bodies are very distinctly different. Compared with hordein, the alcohol soluble porteid of barley, this malt proteid contains about one per cent. more carbon and one per cent. less nitrogen.

ALCOHOL SOLUBLE PROTEIDS.

	Hordein of barley.	Bynin of barley malt.	Zein of maize.
Carbon	54.29	55.00	55.23
Hydrogen	6.80	6.67	7.26
Nitrogen	17.21	16.26	16.13
Sulphur	0.83	0.84	0.60
Oxygen	20.87	21.20	20.78
	100.00	100.00	100.00

MALT PROTEID INSOLUBLE IN WATER SOLUTION AND DILUTE ALCOHOL.

The proteid remaining undissolved, after extracting malt with water, salt solution and alcohol, was not separated or identified, but its presence in considerable quantity was shown, as follows:

After extracting 100 grams of malt first, with ten per cent. sodium chloride solution, and then with alcohol of 0.90 sp. gr., dehydrating with absolute alcohol and drying in the air, a residue was obtained which weighed seventy-five grams and contained 0.82 per cent of nitrogen, equivalent to 0.62 per cent. reckoned on the original malt. Assuming, as is probably true, that this nitrogen belongs to proteid matter, we have in the residue three and eight-tenths per cent. of proteid, insoluble in the reagents named.

SUMMARY.

In the malt used in this investigation we have found:

1. *Bynedestin*, readily soluble in very dilute salt solution, therefore largely passing into the aqueous extracts because of the soluble salts of the seed. This globulin contains two per cent. more carbon and three per cent. less nitrogen than edestin, the globulin of barley, and is much more soluble in very dilute salt solutions than edestin.

The composition of this globulin, as shown by the average of eleven analyses, is:

BYNEDESTIN.

Carbon	53.19
Hydrogen	6.69
Nitrogen	15.68
Sulphur	1.25
Oxygen	23.19
	100.00

Bynedestin, dissolved in ten per cent. sodium chloride solution, gives a turbidity at 65° and a flocculent coagulum at 84°, but, even after heating for some time at 100°, the coagulation is far from complete.

This proteid is not precipitated by saturating its solutions with sodium chloride, and but partly precipitated by saturating with magnesium sulphate.

2. *Leucosin*, an albumin, identical in composition and properties with the leucosin found in wheat, rye and barley. The composition of this proteid was found to be :

MALT ALBUMIN, LEUCOSIN.

Carbon	53.07
Hydrogen	6.72
Nitrogen	16.71
Sulphur, Oxygen	23.50
	100.00

Leucosin is intimately associated with diastase.[1] Heated to 59°, solutions of this proteid become turbid, and at 58° a flocculent coagulum occurs. Coagulation, however, is incomplete unless the solution is heated for some time and the temperature raised to about 70°. Saturation with sodium chloride or with magnesium sulphate partly precipitates leucosin.

3. A *Protoproteose* readily precipitated from aqueous solution by adding an equal weight of alcohol. No preparations of this body were obtained free from albumin. Its composition is nearly the same as that of leucosin, since preparations containing from ninety to fifty per cent. of it, together with from ten to fifty per cent. of leucosin, are not distinguishable by analysis.

4. A *Protoproteose* less readily precipitated by alcohol than the preceding, and of a different composition, as shown by the following figures :

MALT PROTOPROTEOSE.

Carbon	50.63
Hydrogen	6.67
Nitrogen	16.69
Sulphur, Oxygen	26.01
	100.00

[1] See papers on Diastase, Annual Reports of Conn. Agr. Expt. Station, 1894. pp. 202, 204, and 1895, p. 238 ; also this JOURNAL, **17**, 587; **18**, 536.

That this is not an impure preparation of the preceding, is indicated by the fact that the amount of nitrogen is alike in both, while the carbon differs by two per cent. This difference would probably not be caused by non-proteid impurities. It is possible that the deuteroproteose next to be described, may not have been completely separated by the process employed.

5. A *Deuteroproteose* which could not be separated from non-proteid impurities.

6. A *Heteroproteose* in extremely small amount.

7. *Bynin* a proteid insoluble in water and saline solutions, but readily soluble in dilute alcohol. About 1.25 per cent. of this proteid was obtained from the malt, having the following composition:

BYNIN.

Carbon	55.03
Hydrogen	6.67
Nitrogen	16.26
Sulphur	0.84
Oxygen	21.20
	100.00

8. A proteid insoluble in water, in salt solution and in alcohol, amounting to 3.80 per cent. The composition and properties of this proteid we have been unable to determine.

PROPORTIONS OF THE VARIOUS PROTEIDS IN MALT.

Assuming twenty-one per cent. of the total nitrogen of the malt to exist in non-proteid bodies, and admitting the malt proteids to contain on the average 16.3 per cent. of nitrogen, we have, in the malt investigated, a total of 7.84 per cent of proteids.

As already indicated, p. 555, proteid equal to three and eight-tenth per cent. of the malt was insoluble in alcohol and in salt solution.

It was shown on page 553 that 1.11 per cent. of proteid was recovered from alcohol solution, and making allowance for loss, we may place the amount of alcohol-soluble proteid at 1.25 per cent.

Subtracting the sum of the insoluble proteid and the alcohol soluble proteid from the total malt proteids, we have 2.79 per

cent. for proteids soluble in salt solution, *viz.*, globulin, albumin, and proteoses.

The amount of coagulable proteids was found to be 1.50 per cent., consisting of albumin and a part of the globulin. There remains then 1.29 per cent. for the uncoagulated globulin and the various proteoses. We have accordingly, in the malt used for these determinations, approximately:

		Per cent.
Proteid, insoluble in salt solution and in alcohol		3.80
Bynin, soluble in dilute alcohol		1.25
Bynedestin, leucosin and proteoses soluble in water and salt solution	Coagulable	1.50
	Uncoagulable	1.29
Total proteids		7.84

The results of this study show: that, in germination, the proteids of barley undergo extensive changes without acquiring, or before acquiring the properties of proteoses; that hordein disappears and an alcohol soluble proteid of entirely different composition takes its place; that edestin also disappears and a new globulin is formed, very different both in composition and properties. The albumin, on the other hand, appears to be unchanged in its characters, but its quantity is increased. It is to be noted also that hordein and edestin are both replaced by proteids much richer in carbon and poorer in nitrogen.

NOTE.

A Cheap Adjustable Electrolytic Stand.—Stands for electrolytic work, especially for efficient assaying of copper, should fulfill certain conditions.

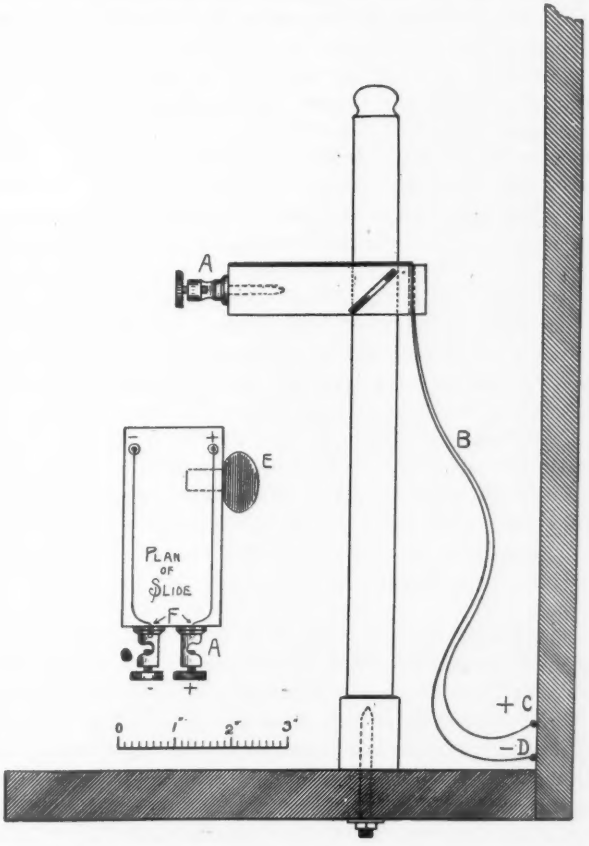
All joints and connections, as far as possible, should be permanently soldered and very few switches used.

If many assays of the same kind are to be simultaneously conducted, each assay should be independent of its neighbor.

The stands or terminals, for holding the platinum cases or cylinders and spirals (which are the forms of electrodes generally used in large laboratories), should be capable of instant adjustment to suit a beaker of any height and size, or permit a block of wood to be placed under the beaker, since some chemists

prefer when an electrolysis is finished, to wash the electrodes by quickly slipping out a block, dropping the beaker, and replacing it with another of distilled water.

The author has designed and used for several years, electro-



lytic stands which are simple in construction and comparatively inexpensive, and a number of them may be quickly turned

out together in any works possessing a carpenter or machine shop.

The drawing shows that the stands each consist of small, turned sticks of oak wood, one foot high, and fastened by a short lag screw, bolt, or common screw and washer, to a wooden shelf one inch thick, under which are placed the gravity or storage batteries.

A block of wood, of the shape and construction given in the sketch, is arranged to slide on the wooden post, and fastened by the large screw (*E*). Into the front end of the sliding block are screwed two brass holders for the "cylinders," or "cone and spiral" electrodes.

All dimensions may be taken from the scale accompanying the sketch. The "single binding posts" given in chemical catalogues, make very good holders if one side of the brass post is filed out opposite the hole as shown in cut (at *A*.)

The cotton-covered (No. 19) connecting wires (*B*) are connected by soldered joints with two parallel main wires (No. 16) at *C*, *D*, and are led up through two small holes at the back of the sliding block and over the top to the brass plugs in front.

These holders or plugs may be screwed in part way, and the bared ends of the wire twisted once around the screw.

The brass plugs are then screwed up tightly in position, the short, free end of the wire bent down over the top in a little slot previously filed, and fastened with a drop of solder (as at *F*.)

These neat, wooden stands may be set in a single or in a double row in a "staggering" position.

The stands may be arranged in little sets of twos or fours, independent of each other, by breaking one of the parallel main wires at *C* or *D* by a switch or removable plug of low resistance.

From each of these groups or sets lead wires with soldered connections may be run to batteries below, and to arrangements of incandescent lamps on the wall above and behind the row of stands, and each group of assays may thus be given a different strength of current, one sixteen candle power lamp being generally sufficient for four copper assays.

The advantage of connecting assays of the same kind in parallel, as indicated in the sketch, consists mainly in the fact

that the current is divided up between the assays, lessening the total resistance, and that any electrode may be quickly removed after loosening the screw at *A* without disturbing the other analyses.

If the laboratory is wired for incandescent (seventy-five volt) lamps, the current obtained from a circuit containing arrangements of sixteen or thirty-two candle power lamps is more steady than that from small batteries.

If the dynamo only runs at night, a bank of lamps in parallel arc may be arranged as a resistance and the current passing through these, caused to charge two or more storage batteries in series at night. In the morning the direct current, through resistance of lamps, which had been applied to analyses during the night, may then be switched off and the dynamo current also switched off from storage cells, which are then connected up, through suitable resistance coils, in an opposite direction with the copper analyses yet unfinished.

As noted, adjustable resistance coils should be included in the circuit of analyses, through which the storage cells discharge. For a description of such apparatus, I refer to the works of well known authorities,[1] [2] and for different arrangements of incandescent lamps to articles in this Journal of 1894 and 1895.

The "chloride accumulator" is thought to be the most efficient storage cell for laboratory work. Three cells in series of the type (5 E, Electric S. Bat. Co., Phila.), require the current of ten sixteen-candle-power lamps in parallel arc to secure a full charge in one night of twelve to fourteen hours, and will, when connected with analyses, give out again for a period of fourteen to fifteen hours about eighty per cent. at two volts potential.

The foregoing descriptions will, it is hoped, be of service to those who have considerable electrolytic work with copper, or other metals, and the stand described is recommended as one that is permanent, easily adjustable and comparatively inexpensive, if set up by the chemist himself.

G. L. HEATH.

[1] Clasen s Quant. Anal. by Elect,, Am. Ed., pp. 23–28.
[2] E. F. Smith's Electrolysis, pp. 27–28.

NEW BOOKS.

WATER SUPPLY (CONSIDERED PRINCIPALLY FROM A SANITARY STANDPOINT). By WILLIAM P. MASON. 8vo. viii, 504 pp. New York: John Wiley & Sons. Price, $5.00.

There is scarcely a subject about which chemists are called upon to give an opinion, which requires broader knowledge, more care in analytical work and, above all, more exercise of good common sense, than the determination of the sanitary character of a water supply.

The present work will be found of service not only to chemists, but also to physicians, engineers, and many others who are called upon to consider problems of this kind.

The author has had a wide practical experience in the study of water supplies and shows excellent judgment selecting that which is most valuable, both from his own experience and from the almost boundless literature of the subject.

In a long chapter on Drinking Water and Disease, a good selection is given from the many cases on record where epidemics, especially of typhoid fever and of cholera, have been proved to have been connected with the use of a contaminated water.

The chapter on the artificial purification of water gives a detailed account of the best systems in use in America and in Europe for the filtration of water on a large scale. A large number of plants of this character have been personally examined by the author.

In discussing the natural purification of water it is interesting to notice that the author agrees with those who believe that the self-purification of a river water which has once been seriously contaminated with sewage is a very slow process, and that such waters should not be recommended for potable use even after many miles of flow. The evidence given on this point seems to be almost incontrovertible.

About one-third of the book is given to the discussion of the various forms of natural waters: rain, ice, snow, river water, stored water, ground water and deep-seated water.

Concise and satisfactory directions are given for the chemical

and bacteriological examination of waters, the latter being confined to methods of preparing culture liquids and counting colonies. In the opinion of the writer the retort which is recommended for the "albuminoid" ammonia process would be better replaced by a flask, or a distilling bulb with a ground glass stopper. The retort seems to have little place left in the modern laboratory.

The opinion is expressed that, while the bacteriological examination is important, its value has been greatly overrated, and the chemical examination will, in most cases, give more reliable information as to the character of a water.

The typography and general arrangement of the book are excellent, and the writer is not acquainted with any other work which contains so much that is of value on the subject.

W. A. NOYES.

HINTS ON THE TEACHING OF ELEMENTARY CHEMISTRY IN SCHOOLS AND SCIENCE CLASSES. By William A. Tilden, D.Sc., F.R.S. London: Longmans, Green & Co. 1895. 12mo. 84 pp. Ill. Price, 75 cents.

Dr. Tilden is one of the English chemists who examines many papers written by candidates in chemistry. He is well qualified, therefore, to speak to teachers of the subject, and his book is practically a series of short talks to teachers. The following extract gives a good idea of his point of view:

"In order to cultivate the powers of observation, various branches of natural science have been brought into use in schools, but none seem to present so many advantages as are offered by chemistry when rightly taught. As a science based entirely upon the results of observation and experiment, it is only by making experiment a principal feature of the system of instruction that these advantages can be secured. The observations and experiments must also, as far as possible, be the work of the pupil and not of the teacher, and therefore exercises undertaken should be in the first instance of the simplest possible character, and graduated so as to lead on to more difficult operations, which should only be undertaken after some time and after demonstration by the teacher. It is a mistake to suppose that the great theories of chemistry can be established by experiments conducted wholly by beginners, but with due preliminary

instruction the more advanced student may get a long way in this direction."

Prof. Tilden seems to fully comprehend the necessity for simplicity in the apparatus to be used by beginners and a number of hints are given in this line worth consideration.

EDWARD HART.

BOOKS RECEIVED.

Bulletin No. 41. Experiments with Wheat and Oats. University of Illinois, Agricultural Experiment Station, Urbana, Ill. 16 pp.

Bulletin No. 42. Corn Experiments. University of Illinois, Agricultural Experiment Station, Urbana, Ill. 18 pp.

Chemistry at a Glance. A Study in Molecular Architecture. By Herbert B. Tuttle. No. 1. Oxides. 1896. 59 pp. Price, 60 cents.

A Dictionary of Chemical Solubilities. (Inorganic.) By Arthur Messinger Comey, Ph.D. London: Macmillan & Co., and New York. 1896. xx, 515 pp. Price $5.00.

Experimental-Untersuchungen über Zersetzung und Verbrennung von Kohlenwasserstoffen. By Fritz Haber. München: R. Oldenbourg. 1896. 116 pp. Price M 1.50.

Elementary Chemistry. By Paul C. Freer. Boston: Allyn & Bacon. 1895. x, 284 pp. Introductory price, $1.00.

Bulletin No. 41. Tobacco. Yellow Leaf and Cigar Varieties. Agricultural Experiment Station, Baton Rouge, La. 32 pp.

Nineteenth Annual Report of the Connecticut Agricultural Experiment Station for 1895. Part II. Fertilizer Experiments. New Haven: Connecticut Experiment Station. 157 pp.

The Liquefaction of Gases. Papers by Michael Faraday, F.R.S., with an appendix. Alembic Club Reprints, No. 12. Edinburgh: Wm. F. Clay. 79 pp. Price, two shillings.

Nineteenth Annual Report of the Connecticut Agricultural Experiment Station for 1895. Part III. Proteids of Potato; of Pea and Vetch; Conglutin and Vitellin. Recent Laws affecting the Station: Index. New Haven, Conn.: Connecticut Agricultural Experiment Station. 88 pp.